Innovations in Cavity Enhanced Laser Absorption Spectroscopy: Using *in situ* Measurements to Probe the Mechanisms Driving Climate Change

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June 24-26, 2003

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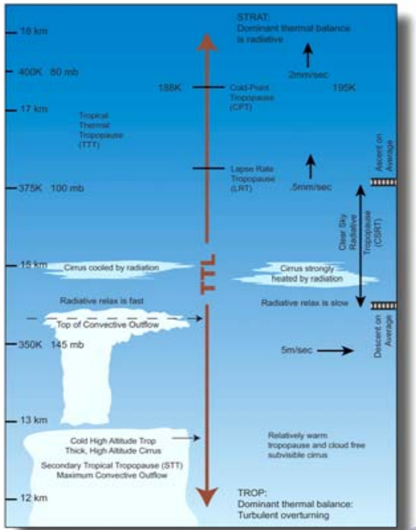
Cambridge, MA 02138

AURA Collaborative Science:

The Union of TC^3, CRYSTAL, INTEX and AVE, and Practical Considerations



TC^3

- Define and understand the chemical boundary condition for the stratosphere with an emphasis on processes that affect ozone
  - Physical mechanisms that control humidity of the stratosphere
  - What is fate of short-lived compounds transported into the tropical upper troposphere?
- Define and understand the response of atmospheric hydrological cycle to climate change
  - What mechanisms maintain the humidity of the tropical and subtropical upper troposphere?
- Are short-lived halogen precursors injected into stratosphere at tropical tropopause?
- Does photolysis of VOCs in tropical UT lead to increased HO_x, formation of PAN, reduction in NO_x/NO_y, reduction in P_{O3}, increase input of NO_y to lower stratosphere?
- How does sulfur enter the stratosphere?

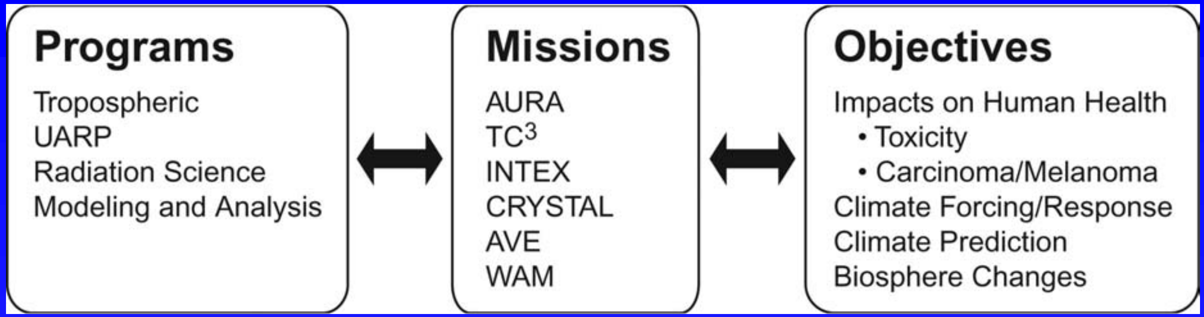
CRYSTAL

- The bottleneck for escape of thermal radiation to space is the structure and distribution of clouds and water vapor in the middle and upper troposphere
  - What is the relationship between global ice and water vapor fields in the TTL and associated radiation fields?
  - How are the kinetics and thermodynamics of cloud formation related to microphysical properties, planetary-scale wave structure and regional-scale convection?
- How is the structure of cirrus anvils tied to convective intensity?
- How do the microphysical and radiative properties of cirrus anvils change through the lifetime of an anvil structure?
- Which processes control the anvil lifecycle?
  - Radiatively driven heating
  - Turbulent mixing
  - Buoyancy, lofting
  - Shear ambient humidity, aerosol composition
- How is the anvil and cirrus structure tied to the chemical composition of the lower boundary of the TTL?

INTEX

- What is the role of convection in coupling the TTL to the boundary layer?
- What is the role of stratospheric input across the subtropical tropopause in the tropospheric budget of ozone?
- What are the relative contributions of photochemical production, photochemical loss, and transport in setting the ozone concentration of the troposphere as a function of altitude, latitude, longitude and season?
- What processes set the source/sink fluxes and production/loss rates for the ozone precursors NO_x, HO_x, hydrocarbons, water vapor and aerosols?
- How important are regional-scale pollution events to the photochemical structure of the tropical troposphere and to what degree are these pollutants convected into the TTL?
- How can we wisely link an innovative modeling strategy to new observational approaches that couple in situ and remote techniques?
- What combination of mechanisms determines the vertical and horizontal distribution of ozone in the TTL?
- What combination of mechanisms determines the strong longitudinal/seasonal gradients of ozone in the tropical tropopause?
- How are the distributions of ozone and water vapor linked in the tropical tropopause?
- Can we reliably model the lower boundary conditions on the TTL based on a successful representation of NO_x sources (lightning, biomass burning, continental/industrial, etc.), organic sources, water vapor and sulfate sources?

Introduction



Fresh Appraisal

- Spatial and temporal variability of system(s) under study
- Frequency of observations, complexity of missions, instruments and platforms
- Critical role played by new technology
- The rate at which prominent questions are being answered on timescales responsive to societal objectives
- The implications of pervasive under-sampling on the clarity of (and timescale to reach) scientific conclusions
- The degree to which we understand the connection between remote and *in situ* observations
- The complementary nature of:
  - global maps from satellites *versus*
  - *in situ*/remote observations from aircraft and balloons tied to Eulerian and/or Lagrangian models on the regional scale

Overview of Scientific Questions

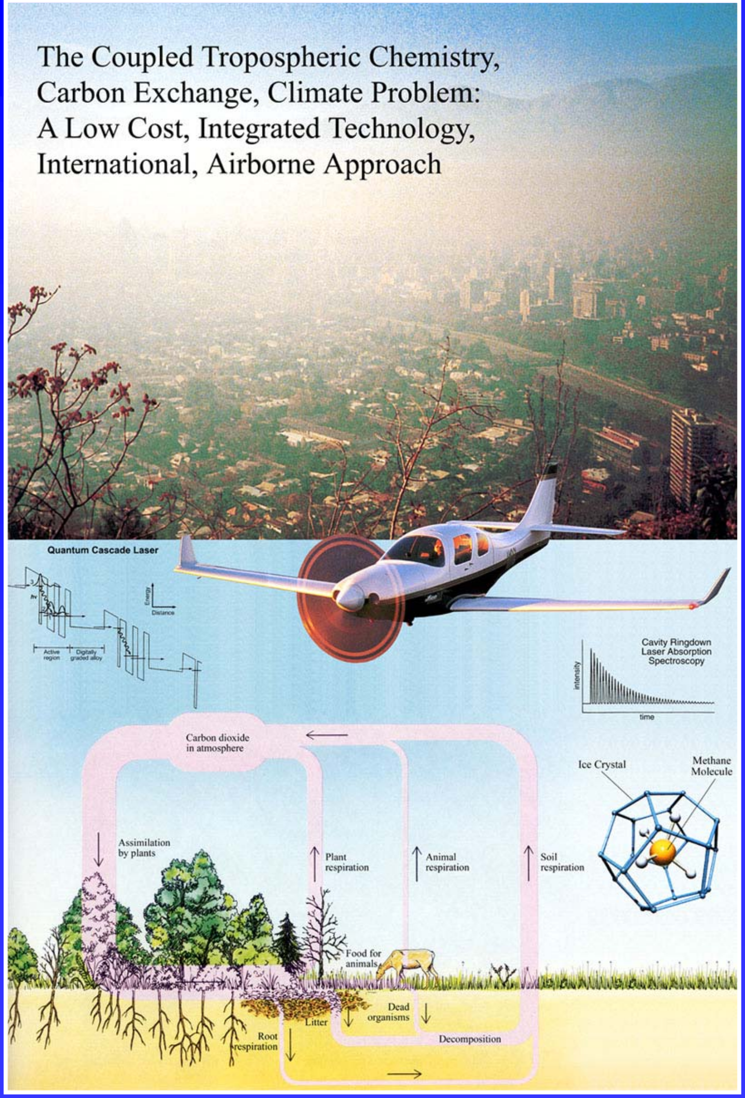
1. With increasing concentrations of infrared active gases and increasing aerosol loading, forecasts of climate change that are tested and trusted must be developed—What strategy is required?
2. How will human health be affected by nitrate, sulfate, organic, heavy metal, and soot emission from urban/regional centers in the developed and developing countries in the next decade?
3. Large losses of ozone over high latitudes have been observed and the cause identified. Why has ozone decreased over midlatitudes of the NH? Will UV dosage levels increase over the next two decades?

IIP Program

- **ICOS, CAPS and CRDS:**
  New techniques for precise, low cost, airborne, *in situ* mapping of species for AURA collaborative science

FOUNDATION

1. Couple problems of urban/regional tropospheric chemistry, carbon exchange, and climate with AURA collaboration
2. Dramatic developments in miniature laser systems
3. Need to couple next generation of trajectory modeling in the troposphere with markedly increased observational coverage using mixed *in situ* and remote sampling methods



In-situ atmospheric measurements are required for understanding:

- Chemistry
  - tropospheric: pollutant plumes
  - stratospheric: ozone depletion
- Transport
  - fine-scale pollution transport
  - convective transport
  - microphysics and water vapor redistribution
- Chemical sources and sinks
  - anthropogenic emissions
  - biogeochemical cycles

Improved measurement sensitivity is especially needed for:

- Trace pollutants and reaction intermediates
  - e.g. formaldehyde, hydrogen peroxide
- Isotopic ratios
  - e.g. CH_3D / CH_4, HDO / H_2O, $^{15}N^{14}NO$ / N_2O
- Radicals
  - e.g. NO_2

Candidate molecules

Molecule
OH, HO_2
NO
NO_2
$HONO_2$
HCl
O_3
H_2O, HDO
CO
$^{12}CO_2$, $^{13}CO_2$
H_2CO
CH_4, N_2O

Future *in-situ* science needs will require instrumentation that is:

NASA's DC-8

payload: 30,000 lb
cost: $25,000 / hr

Cessna Citation

payload: 1800 lb
cost: $2500 / hr

- enhanced in sensitivity
- reduced in weight and volume
- low-cost, readily deployable
- widely applicable technique

Why Cavity Based Absorption Techniques ?

Method	**Sensitivity [/cm√Hz]**	MDL* pptv NO_2 /s	Author
CAPS	**$5x10^{-5}$**	$3.7x10^{7}$	Herbelin
TDL	**$4x10^{-10}$**	2800	Typical
ICOS	**$1.8x10^{-10}$**	1334	Paul
CRDS	**$1x10^{-10}$**	741	Meijer
CRDS	**$2.7x10^{-11}$**	200	This work
AL-CRDS	**$8.8x10^{-12}$**	65	Spence
AL-CW-CRDS	**$1x10^{-14}$**	0.07	Ye
LIF	**N/A**	5	Perkins

*Minimum Detectable Limit: @ 585nm 1m cell (100 passes TDL) 100 Torr

Goals:

- Retain robustness
- Employ passive techniques
- Push sensitivity limits
- Miniaturization / Simplification

→ State-of-the-art technology

Cavity Ringdown Laser Absorption Spectroscopy

Cavity Ringdown Laser Absorption Spectroscopy: History, Development, and Application to Pulsed Molecular Beams

J. J. Scherer, J. B. Paul, A. O'Keefe, and R. J. Saykally
Department of Chemistry, University of Berkeley, California 92720,
and Los Gatos Research, 1685 Plymouth Way, Mountain View, California 94043

Chemical Reviews **97**, 25–51, 1997

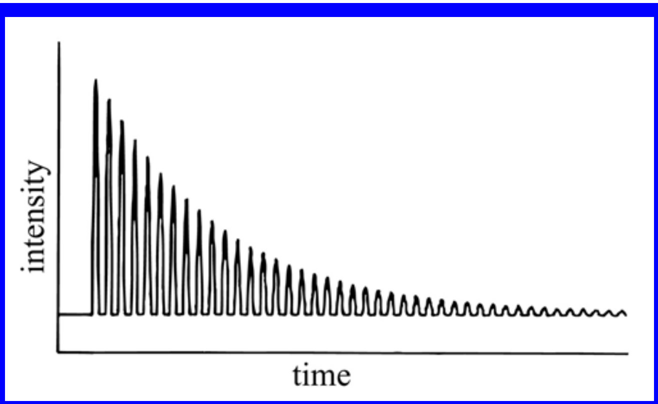


Figure 1. In the short pulse limit, discrete pulses of laser light leak out of the cavity with each pass. The intensity envelope of the resultant decay is approximated by a smooth exponential expression. Determination of the decay time allows the cavity losses or molecular absorption to be determined. Typical cavity decays consist of ten thousand such pulses.

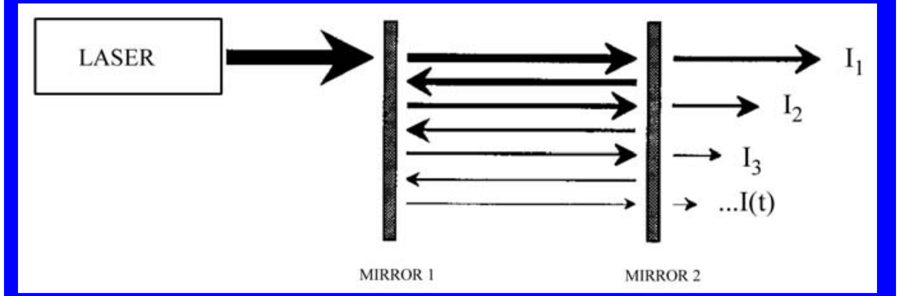
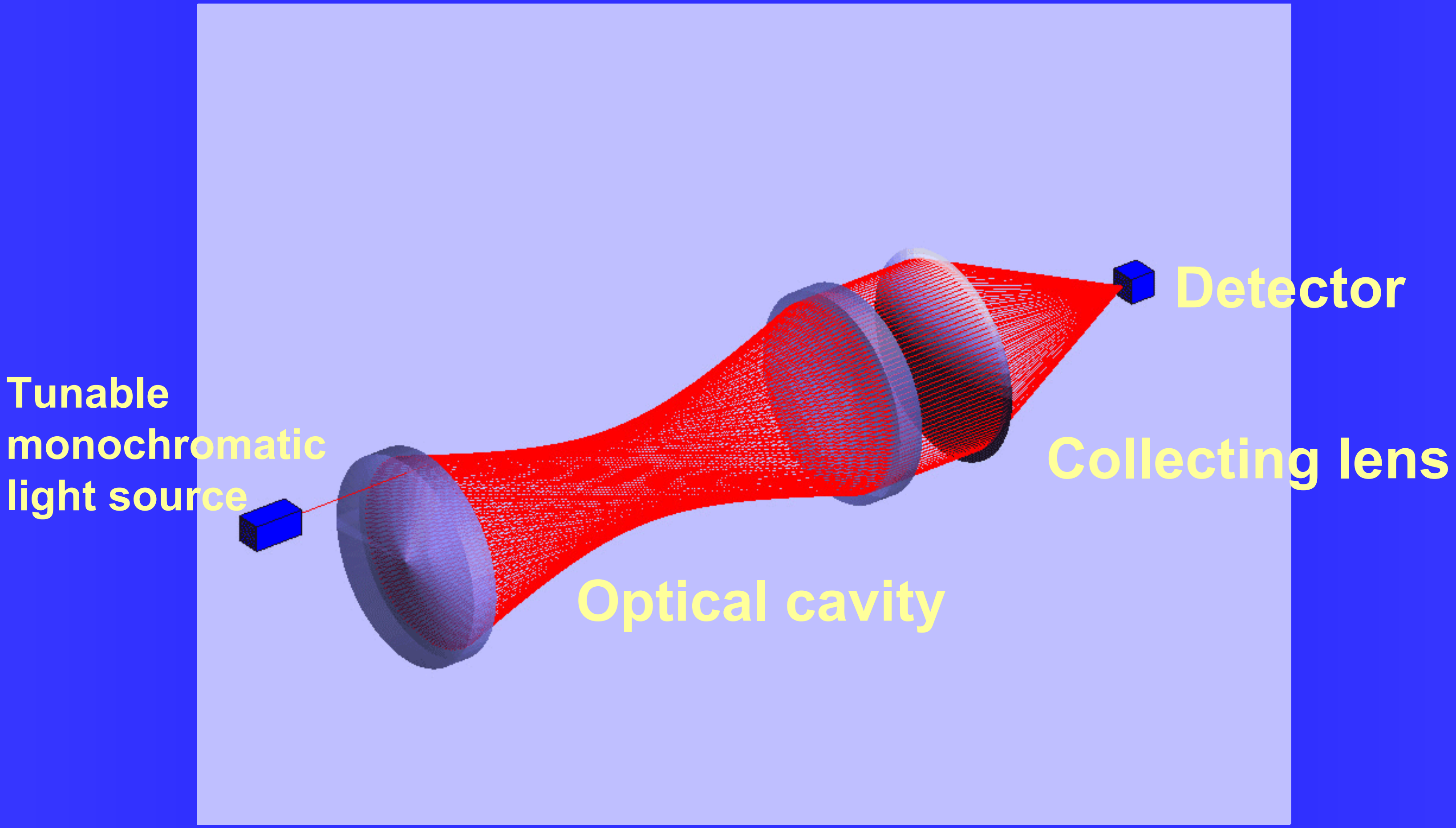
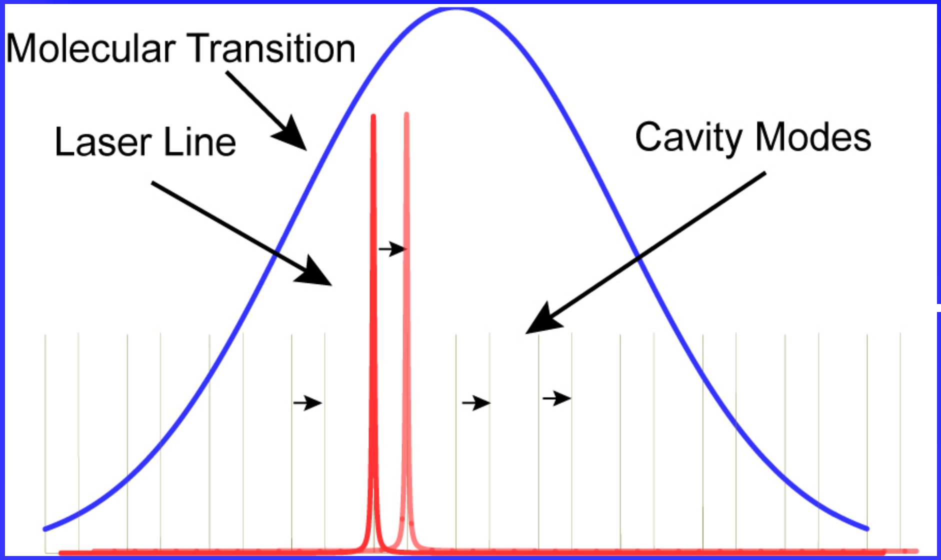


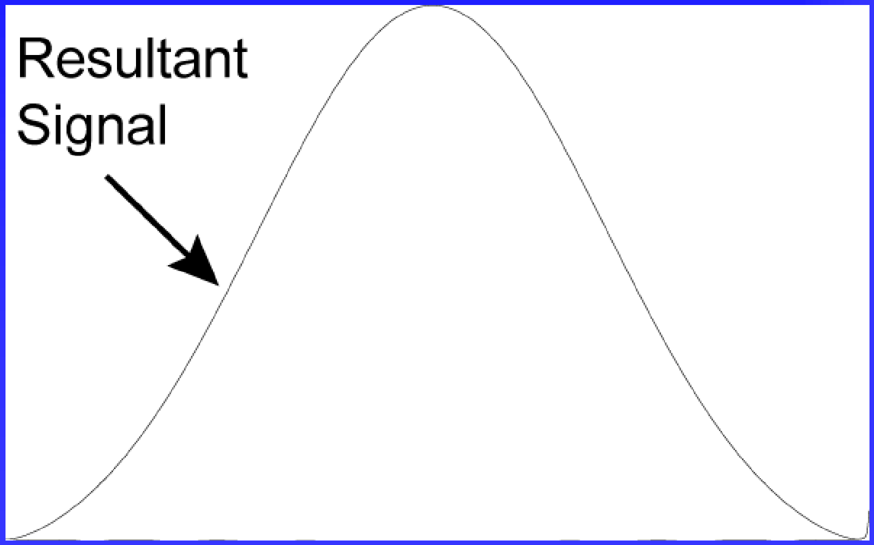
Figure 4. First-order picture of the cavity decay. Because the laser light is incoherent over the dimensions of the cavity, the light acts like a particle as it bounces back and forth between the mirrors. The intensity monitored at the output mirror is therefore simply a function of the single pass transmission coefficient of the cavity.

Optical cavity based absorption spectroscopy

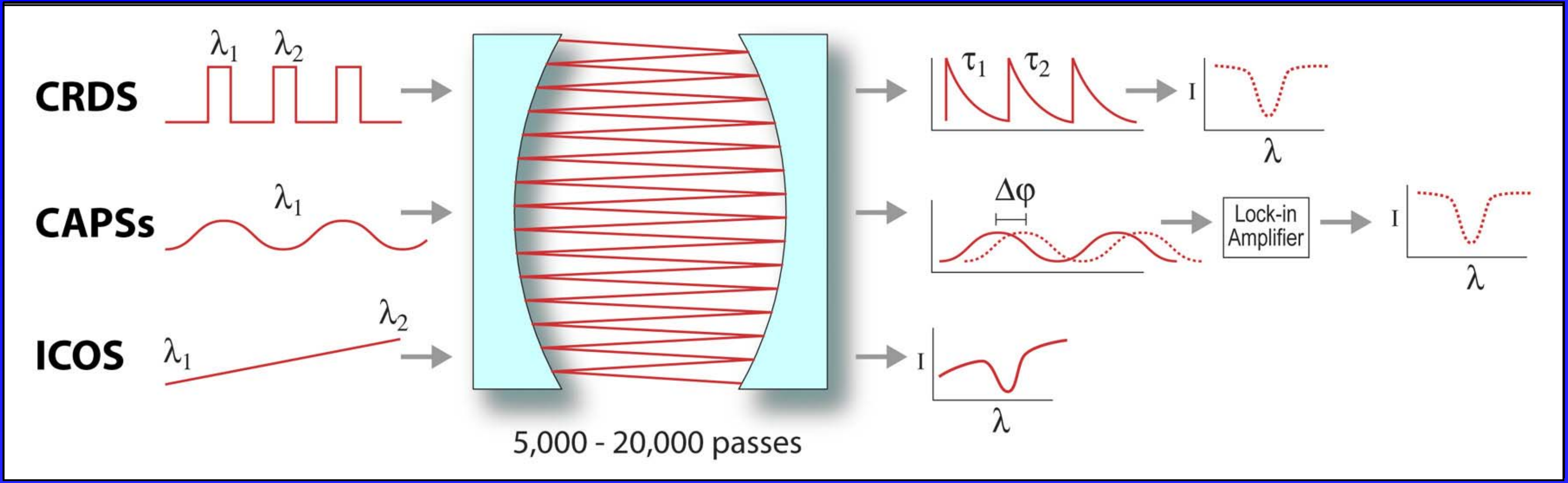


Actively locked optical cavities





Passive cavity absorption techniques



CRDS

Anderson, D., J.C. Frisch, and C.S. Masser. *App. Optics* **23**, 1238, 1984.

O'Keefe, A. and D.A. Deacon. *Rev. Sci. Instrum.* **59**, 2544, 1988.

Romanini, D. and K.K. Lehmann. *J. Chem. Phys.* **99**, 6287, 1993.

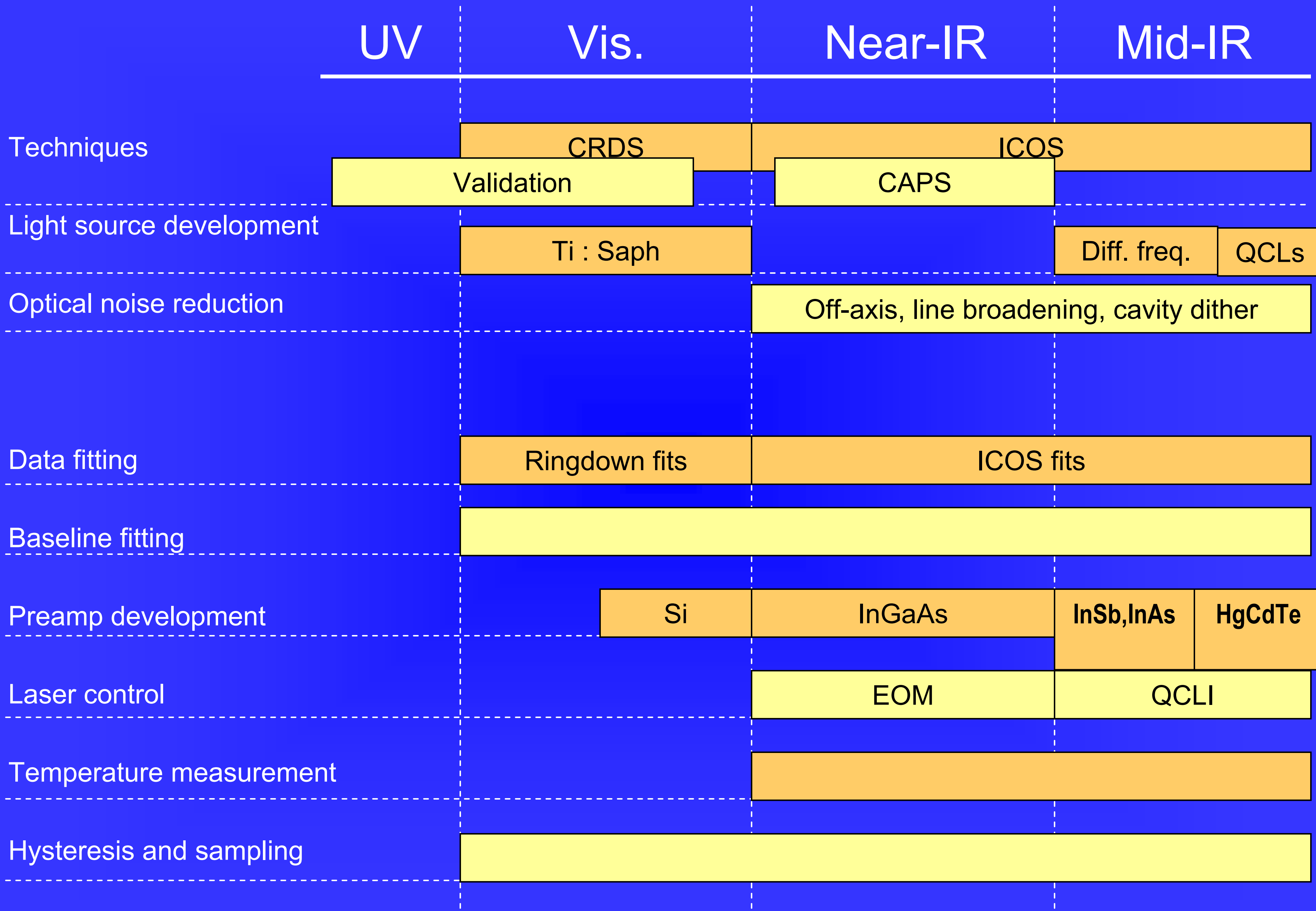
CAPSs

Kwok, M.A., J.M. Herberlin and R.H. Ueunten. *Opt. Eng.* **21**, 979, 1982.

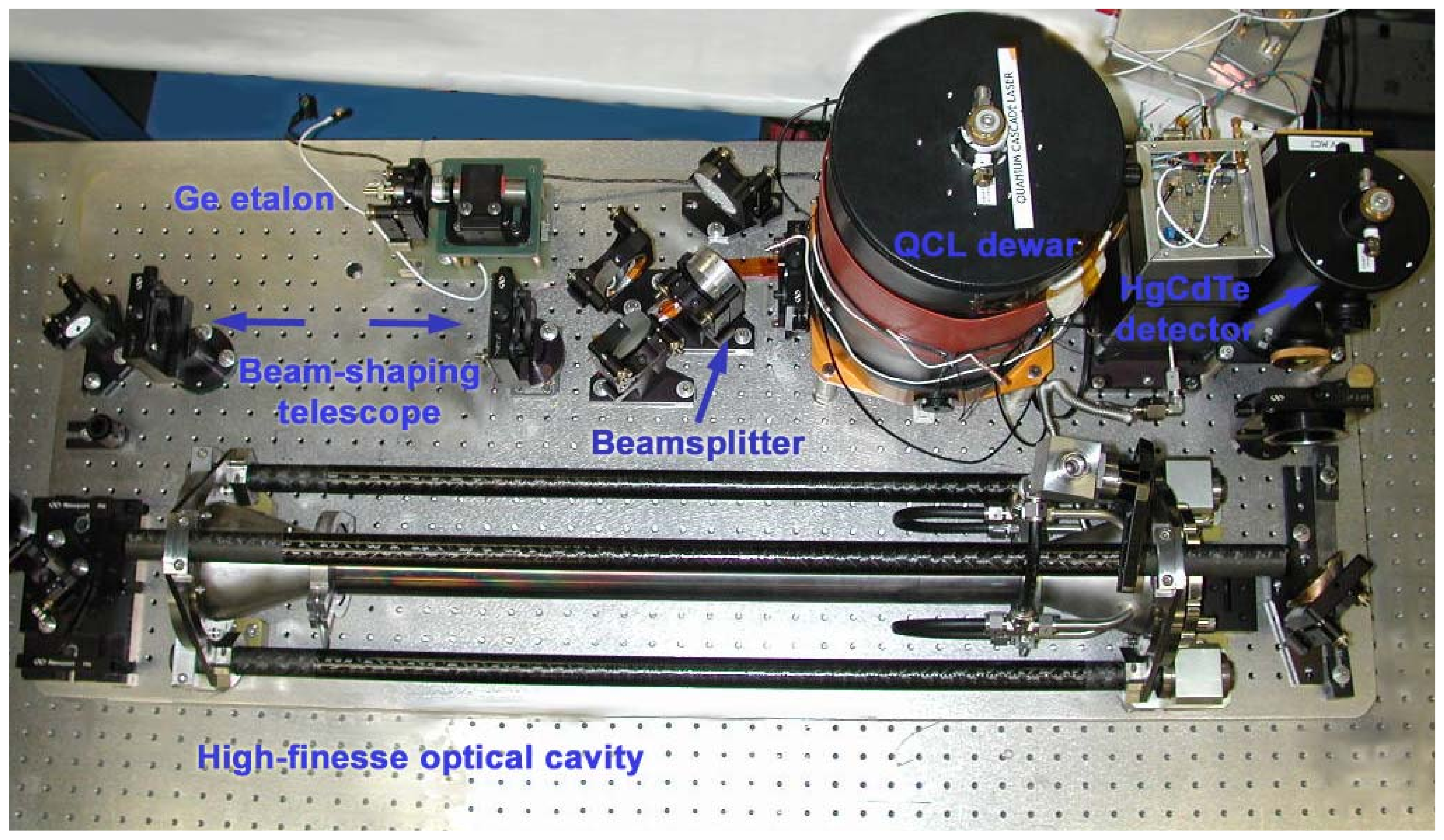
ICOS

O'Keefe A., J.J. Scherer, J.B. Paul *Chem. Phys. Lett.* **307,** 343, 1999.

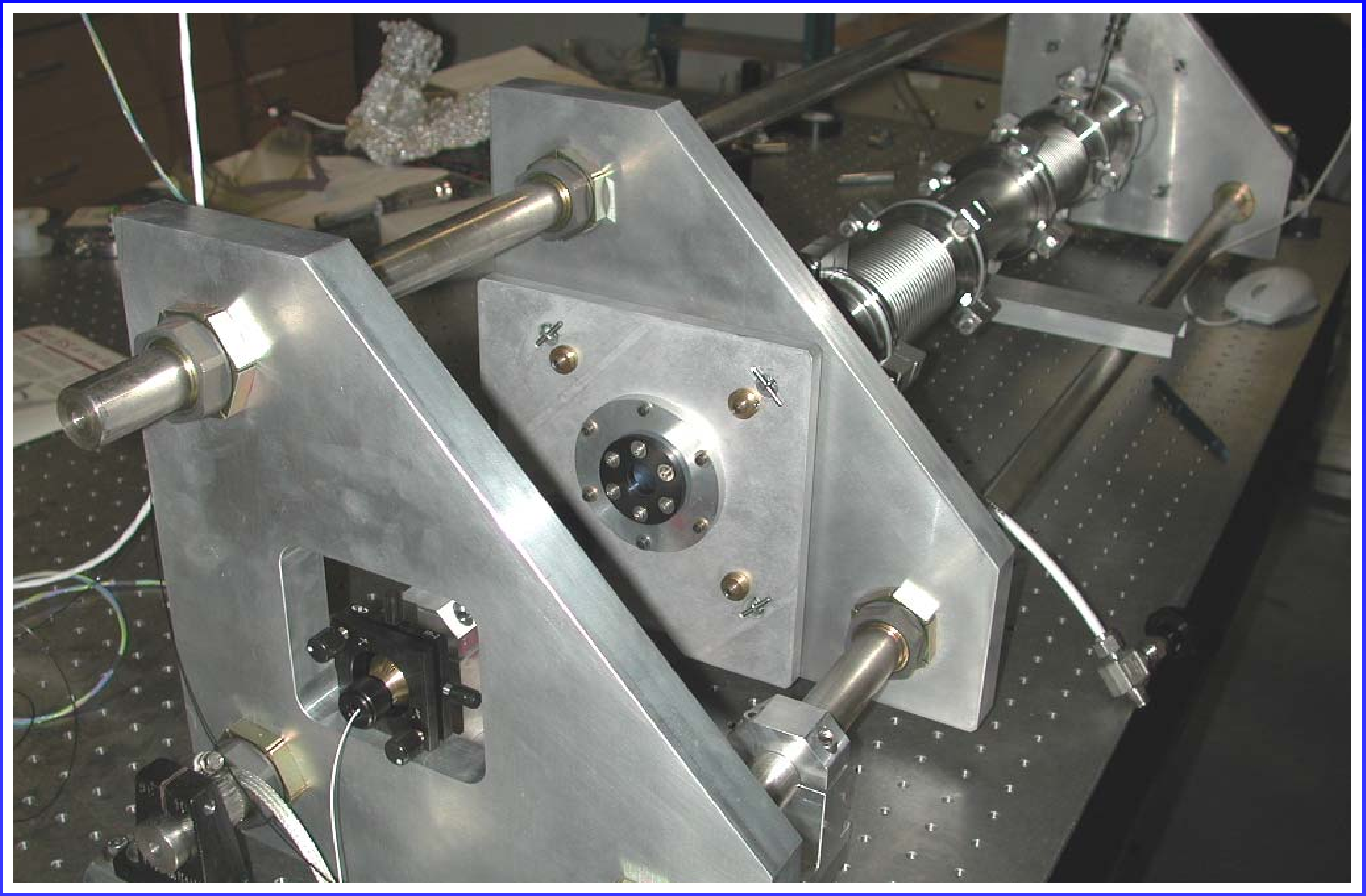
Paul, J.B. L. Lapson, J.G. Anderson. *App. Optics* **40**, 4904, 2001.


UV
Vis.
Near-IR
Mid-IR
Techniques
CRDS
ICOS
Validation
CAPS
Light source development
Ti : Saph
Diff. freq.
QCLs
Optical noise reduction
Off-axis, line broadening, cavity dither
Data fitting
Ringdown fits
ICOS fits
Baseline fitting
Preamp development
Si
InGaAs
InSb,InAs
HgCdTe
Laser control
EOM
QCLI
Temperature measurement
Hysteresis and sampling

Mid-IR development bench (2.5 – 8 μm)



Near-IR development bench (1.5 – 1.8 μm)



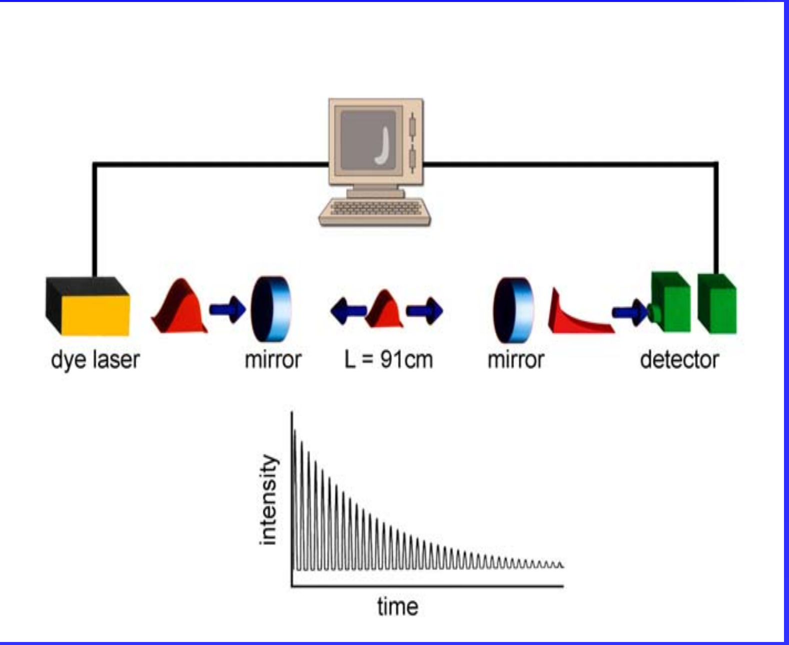
Development project end goal

Demonstration of sensitive *in-situ* measurement of a target molecule using cavity-based absorption spectroscopy, from NASA's WB-57F high altitude research aircraft.

Cavity Ringdown Spectroscopy

Development Platform:

- Light Source:
  - Tunable dye laser @ 585nm (NO_2-LIF)
  - Bandwidth < 0.06 cm^{-1} = 1800 MHz
  - 35 μJ /pulse
  - Repetition rate < 10 kHz
- Cavity / Coupling into Cavity:
  - L = 91cm, R = 99.99615 %, τ ~ 79μs
- Detection:
  - PMT with 585 nm interference filter
  - Electronic filtering and amplification
- Data Acquisition:
  - 14 bit, 50 MHz A/D
  - Software design with high demands on flexibility

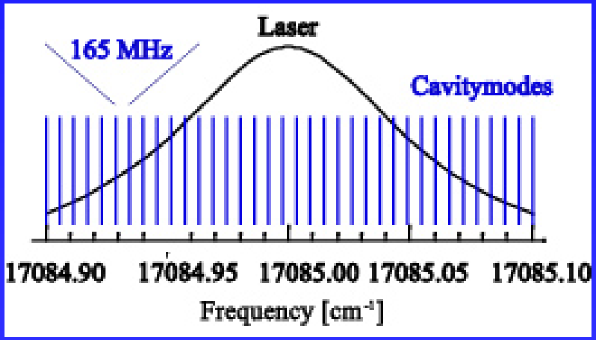


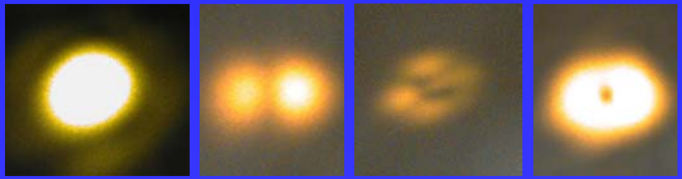
$$\tau = \frac{L}{c\left(1 - R + \alpha L\right)}$$

$$Signal = Ae^{-\frac{t}{\tau}}$$

Light Source

Parameter	Expected Influence on precision and accuracy
Power	amplitude fluctuations
Repetition Rate	overlapping ringdowns → fluctuating baseline
Coupling to longitudinal cavity modes: - Laser Bandwidth - Frequency Stability	amplitude fluctuations
Coupling to transverse cavity modes: - Pointing - Transverse Laser Modes	amplitude and τ fluctuations



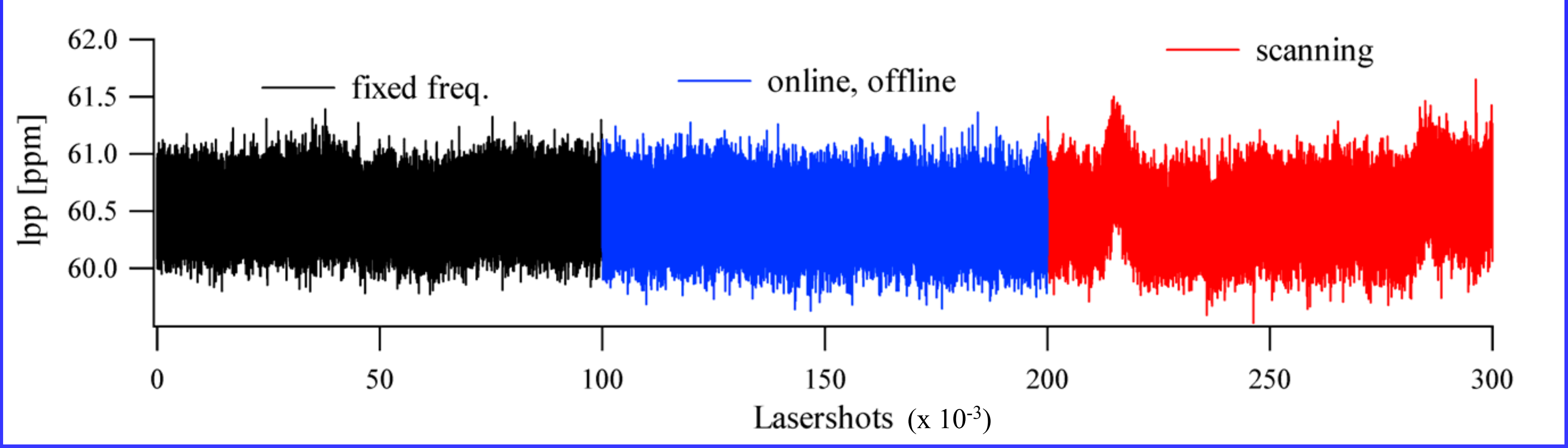


TEM_{00} TEM_{10} TEM_{11} $TEM_{??}$

Coupling Into Cavity

Parameter	Effect	Solution
Transverse mode changes	τ + (ampl.)	Mode matching
Pointing direction	τ + (ampl.)	Fiber coupling
Feedback to laser	ampl. + τ	Off-axis alignment; fiber or spatial filter
Mirror etalon	τ + (ampl.)	Increased mirror wedge
Mechanical Stability:		
- cavity mode structure	**ampl. + (τ)**	**Robust mechanical design**
- coupling	**τ + (ampl.)**	**Fiber coupling**

Fiber coupling minimizes coupling instabilities:

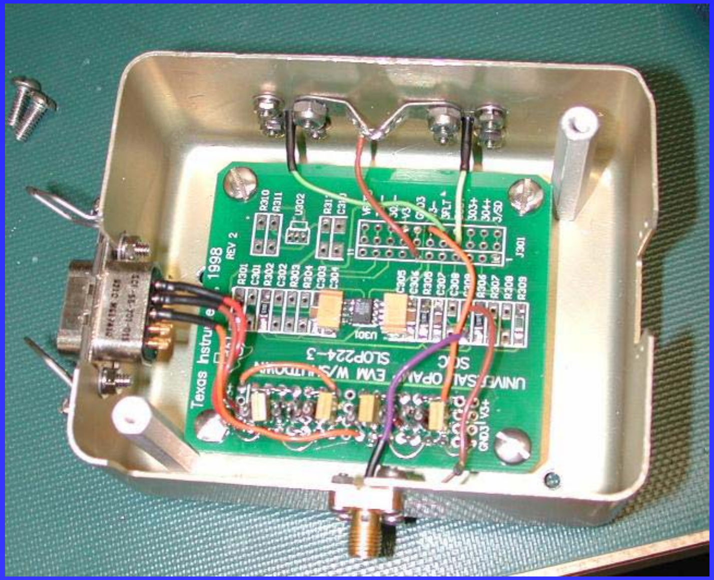


Detection: Detector Requirements

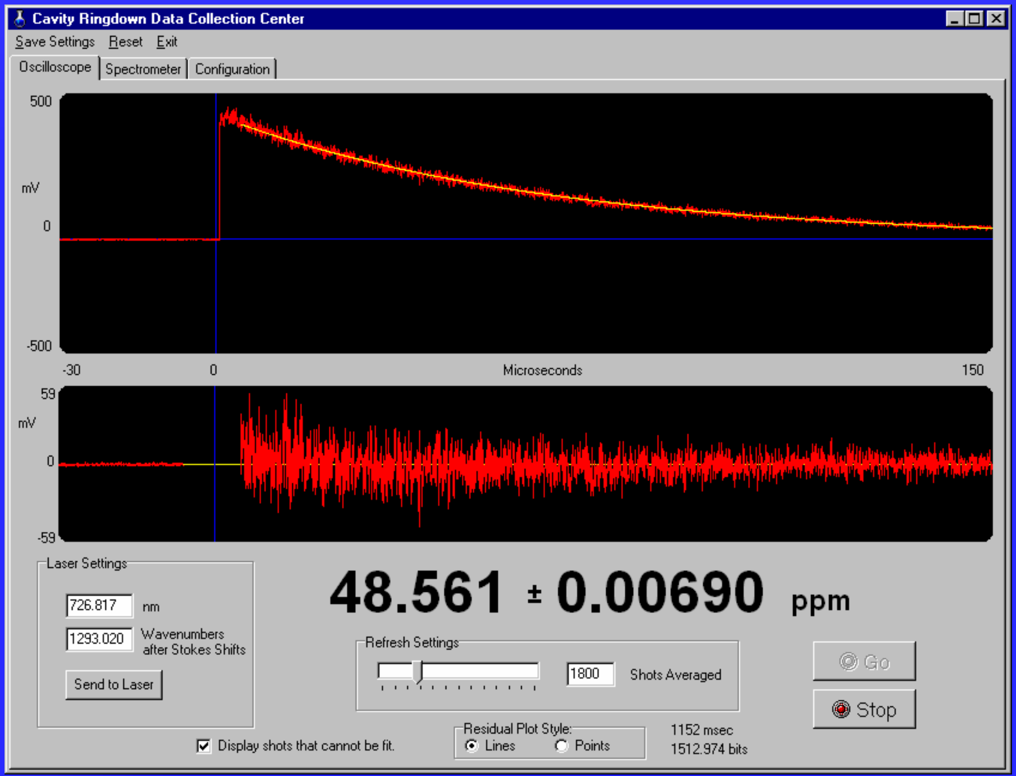
- Fast detector
- Linear
- Limited optical bandwidth
- Commercial PMT with interference filter

Detection: Preamplifier Requirements

- High gain
- Electronic filtering: match bandwidth
  - 25 MHz, x10 gain
  - filtered output 5-10 MHz
- Low ripple power supplies



Data Acquisition Requirements



- Signal properties:
  - Fast rise-time
  - High data rate
  - Amplitude noise

Data Acquisition

A/D Requirements:

- Real time single shot fits
- Oversampling

↓

14 bit 50 MHz A/D

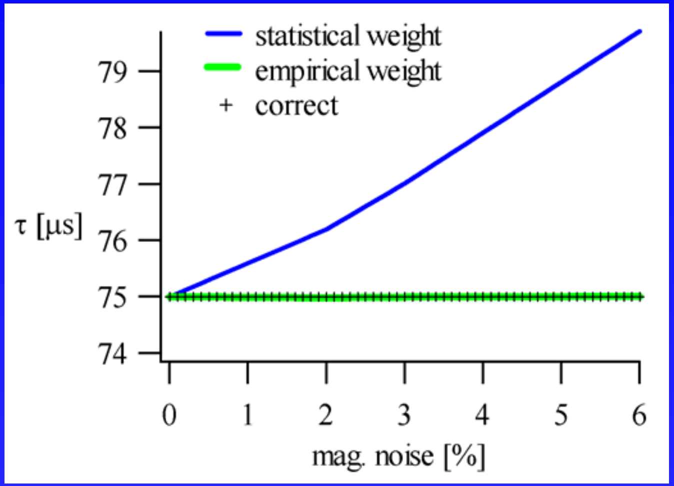
Software Requirements:

- High accuracy
- High precision

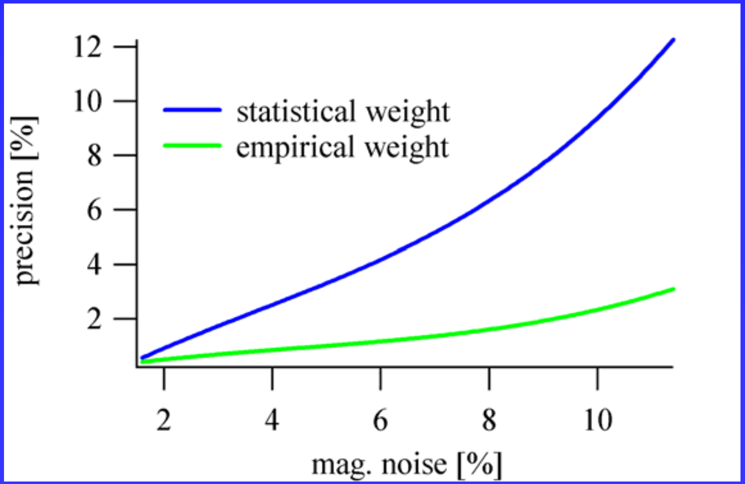
↓

- Linear least squares fit of $ln(y) = -t/\tau$
  - Statistical weight: y^2/σ^2
  - Empirical weight: $y^{0.45843}/\sigma^2$

Accuracy



Precision



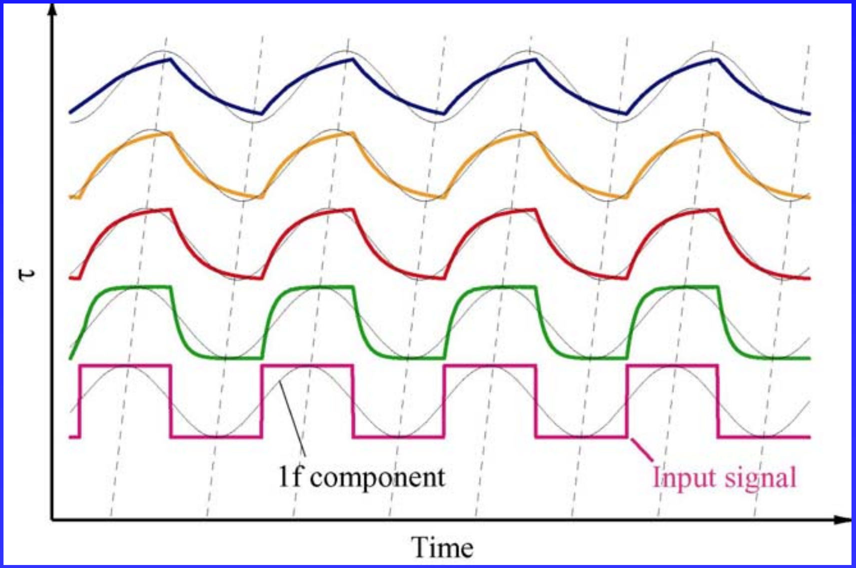
CRDS accomplishments

- **Sensitivity comparable to actively locked results**
  ($2.7 \times 10^{-11}/\mathrm{cm}\sqrt{\mathrm{Hz}}$)
- Understand all significant noise sources
  - Fiber coupling
  - Bandwidth and gain optimized preamplifier
  - Real-time fitting software
- Will allow transfer to mid-IR when light sources are available

Cavity Attenuation Phase Shift (CAPS) Spectroscopy

Why CAPS ???

- CRDS requires pulsed lasers
- Near- and Mid-IR lasers are cw ⟶ chopping results in low pulse power
- Modulation instead of chopping ⟶ CAPS
- New digital lock-in technology
- EOM technology has improved



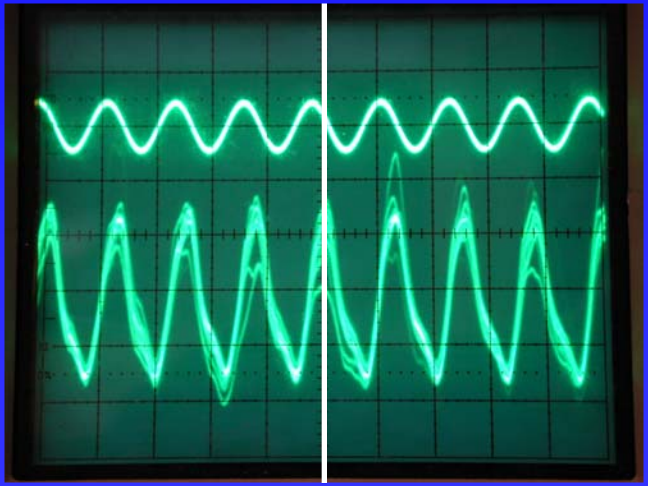
Principle:

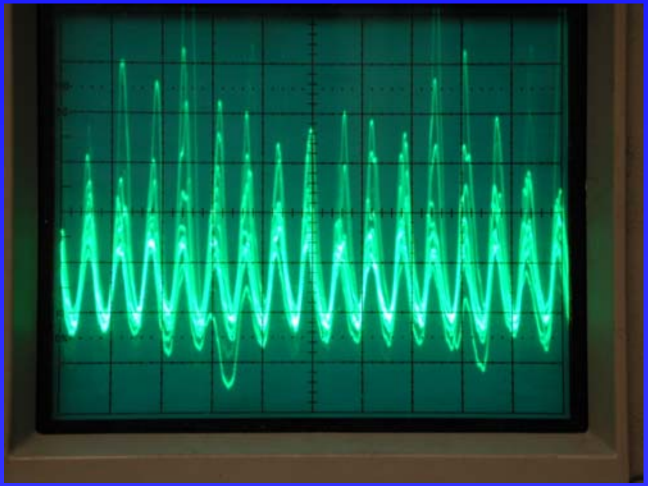
- Intermediate between pulsed CRDS and cw ICOS
- Use cavity as low-pass filter in analogy to electronic RC filter
- Measure phase shift at the 3dB point
- Absorption results in additional phase shift
- Absorbance is determined by input frequency and phase shift

Results

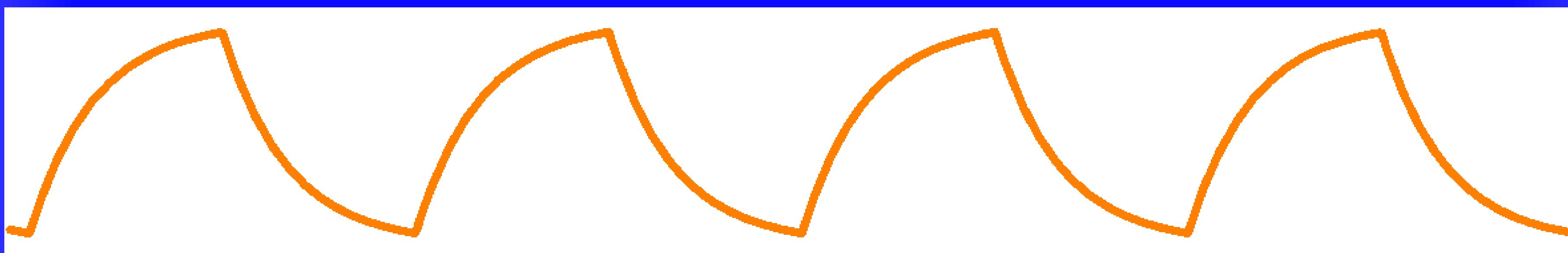
Sensitivity limits determined not by method but technology:

- DSP Lock-in: **Phase resolution low**
- Cavity configuration: **Cavity resonances**





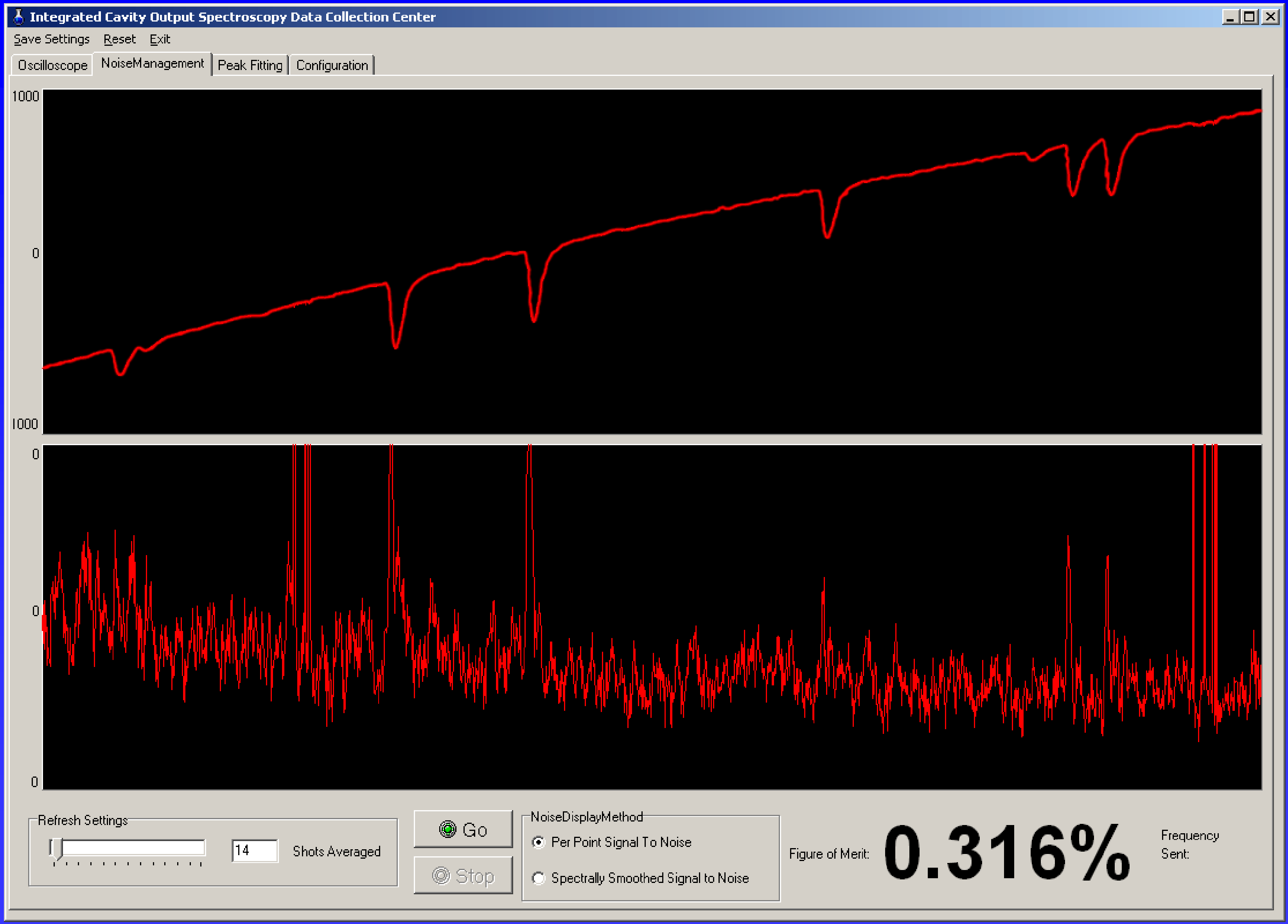
Integrated Cavity Output Spectroscopy (ICOS)



- Steady state transmitted intensity is proportional to absorption in the cavity amplified by reflectivity of the mirrors.

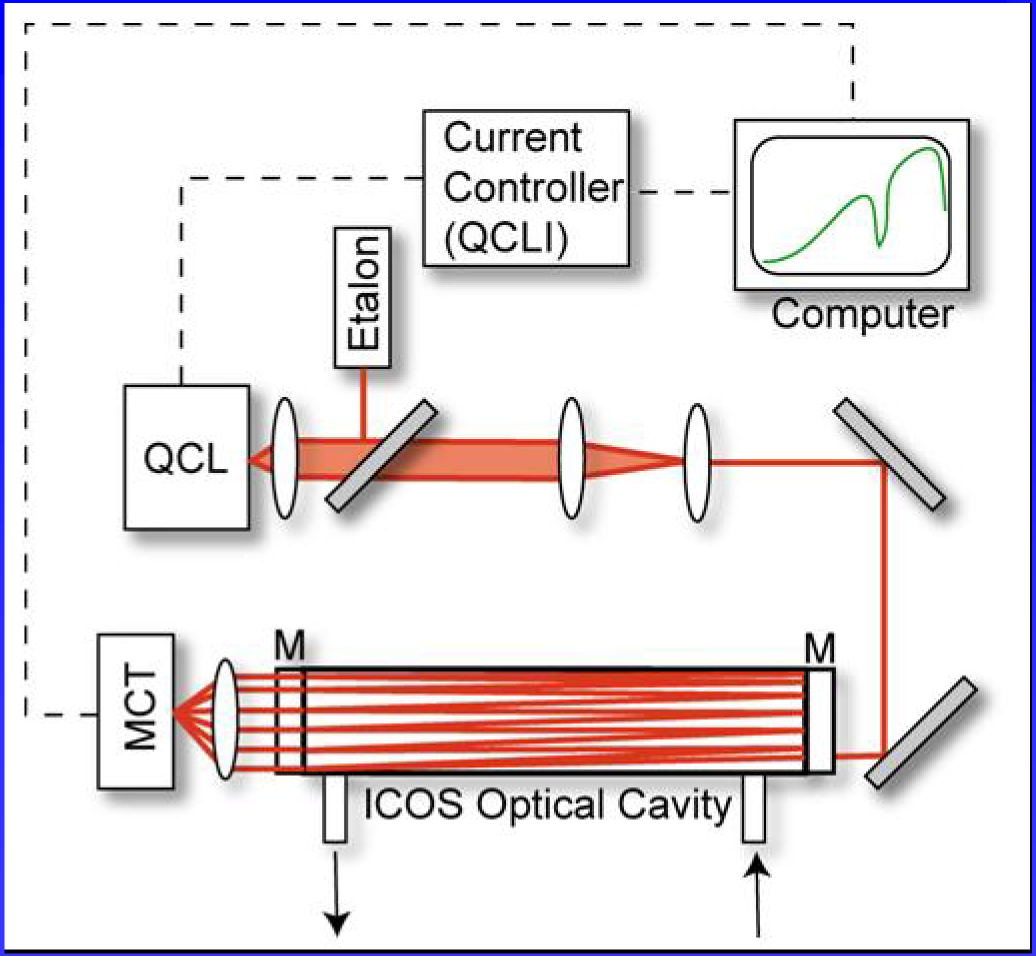
$$I = \frac{P \quad T^2 \quad L}{2c(1 - R + \alpha L)}$$

ICOS Signal


Integrated Cavity Output Spectroscopy Data Collection Center
Save Settings
Reset
Exit
Oscilloscope
NoiseManagement
Peak Fitting
Configuration
1000
0
1000
0
0
0
Refresh Settings
14
Shots Averaged
Go
Stop
NoiseDisplayMethod
Per Point Signal To Noise
Spectrally Smoothed Signal to Noise
Figure of Merit:
0.316%
Frequency
Sent:

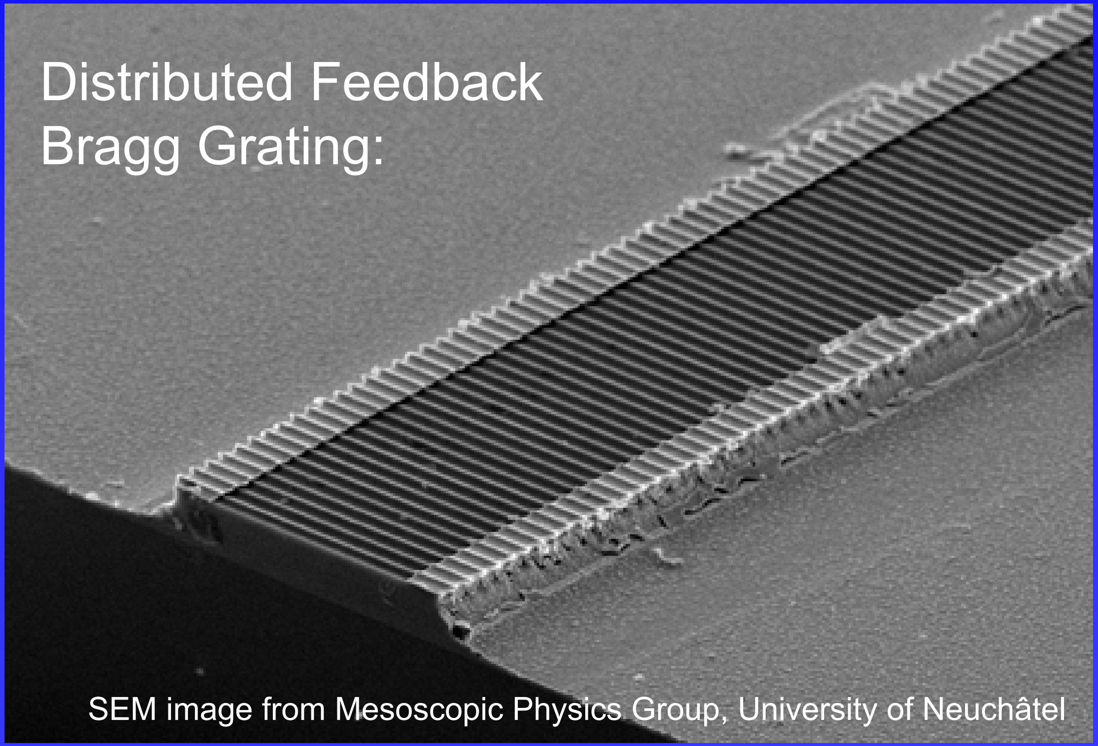
ICOS Instrumental Details

- Light Source
  - Mid IR Quantum Cascade Laser (QCL) or
  - Near IR DFB Laser
- Cavity
  - Stable Optical Cavity
- Detector
  - HgCdTe diode (4-8 µm)
  - InAS diode (2-4 µm)
  - Si, InGaAs Photodiode (400nm- 2µm)
- Data Analysis
  - Analog to Digital Conversion
  - Fitting software



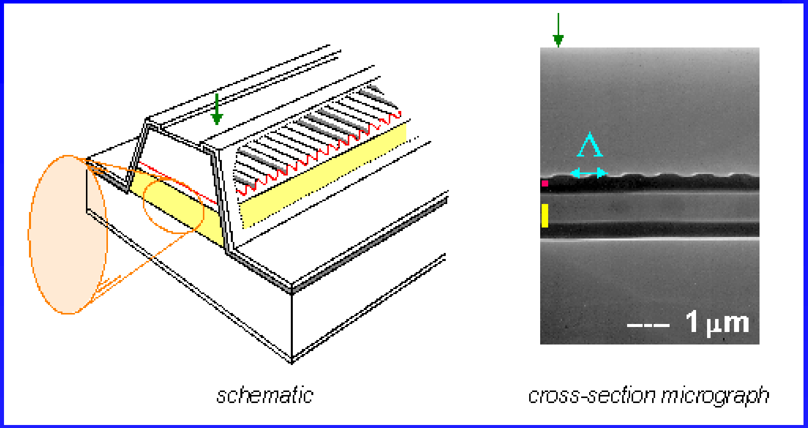
Light Sources

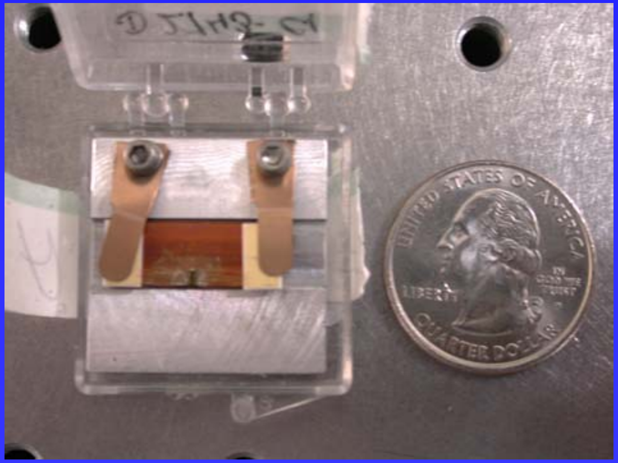
- Continuous wave (cw) Sources
- Continuously tunable over the region of interest
- Narrow linewidth compared to molecular absorptions
- High power output
- Stable power output

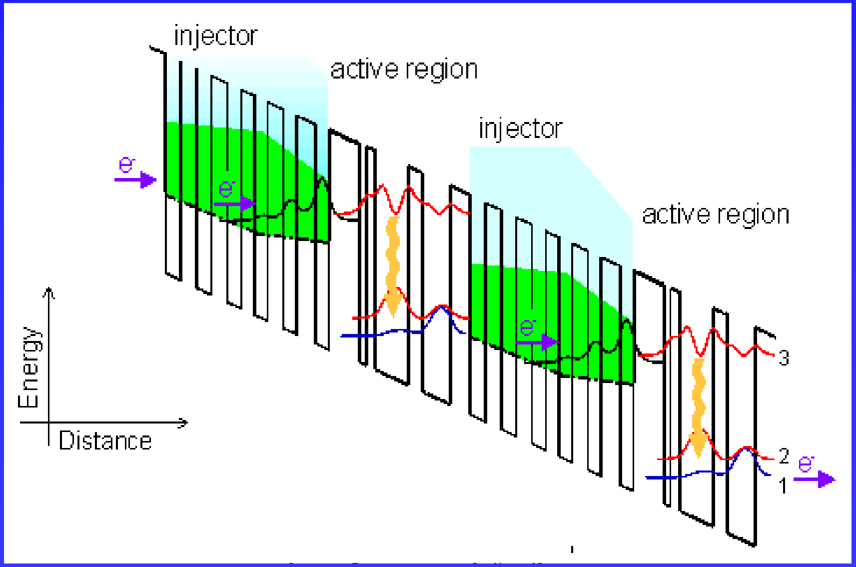


Mid-IR Light Source

- Quantum Cascade Lasers (QCL) (4-17 μm)
  - Benefits:
    - High power (10-160mW)
    - Single mode operation
    - 2 cm^{-1} tuning range
  - Demands:
    - High current device
    - Liquid nitrogen cooling
    - Stable current supply needed







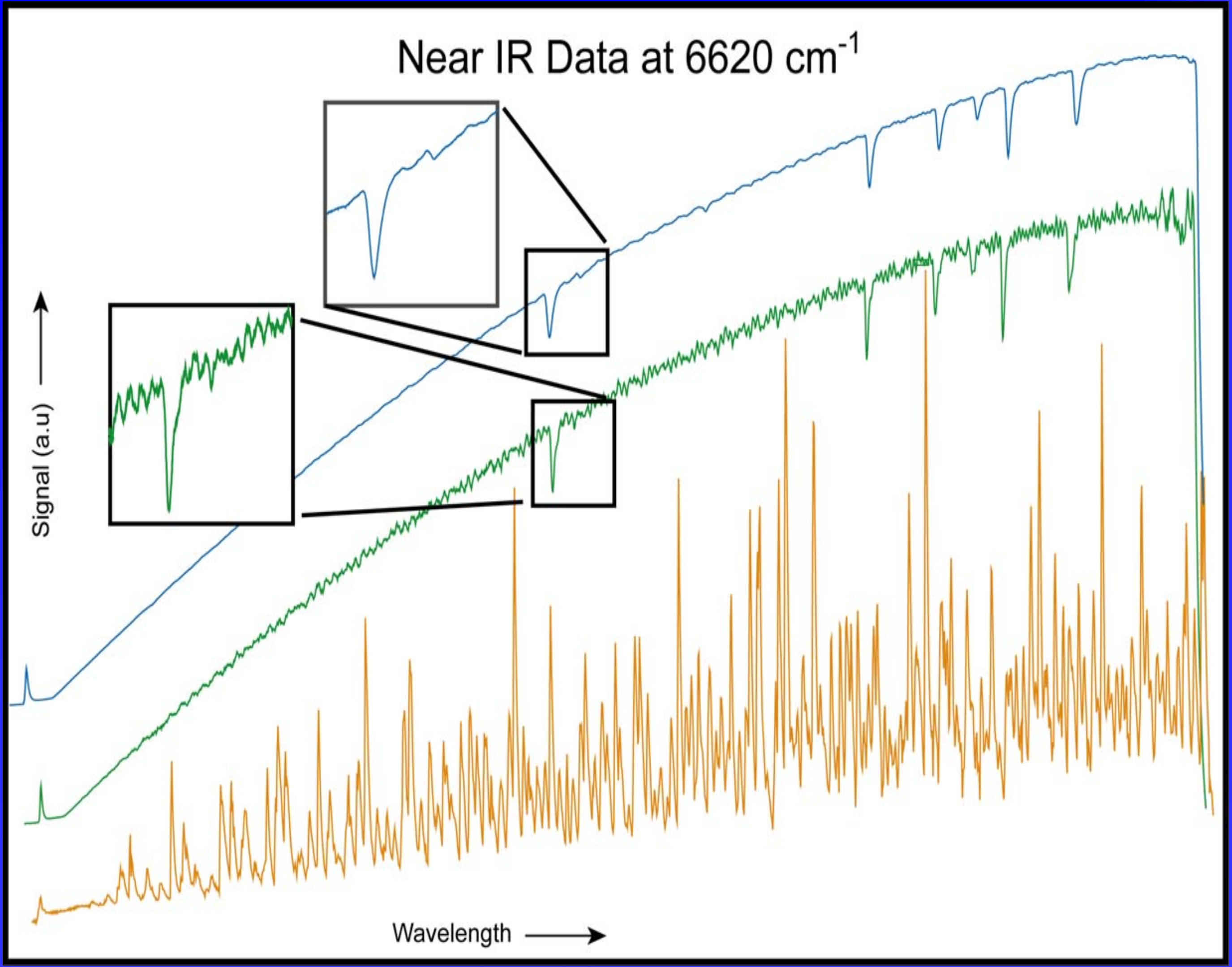
J. Faist, F. Capasso, C. Sirtoni, D.L. Sivco, N. Baillargeon, A.L. Hutchinson, S.N.G. Chu, and A.Y. Cho, *Appl. Phys. Lett*. **68**, 3680-3682 (1996)

Near-IR Light Source

- DFB lasers (1200-1650 nm)
  - Benefits:
    - Widely available for communications
    - Narrow Linewidth (3 MHz)
    - Inexpensive
    - Thermoelectric cooling
    - Fiber Coupled
    - Efficient & Reliable
  - Demands:
    - All components commercially available.

Spurious Coupling to Optical Resonances

- Degrades signal quality
- Scales linearly with Laser Power
- Worst for “on-axis” alignments
- Worst with highly reflective mirrors
- Reduced by vibration
- Reduced by faster scan speeds

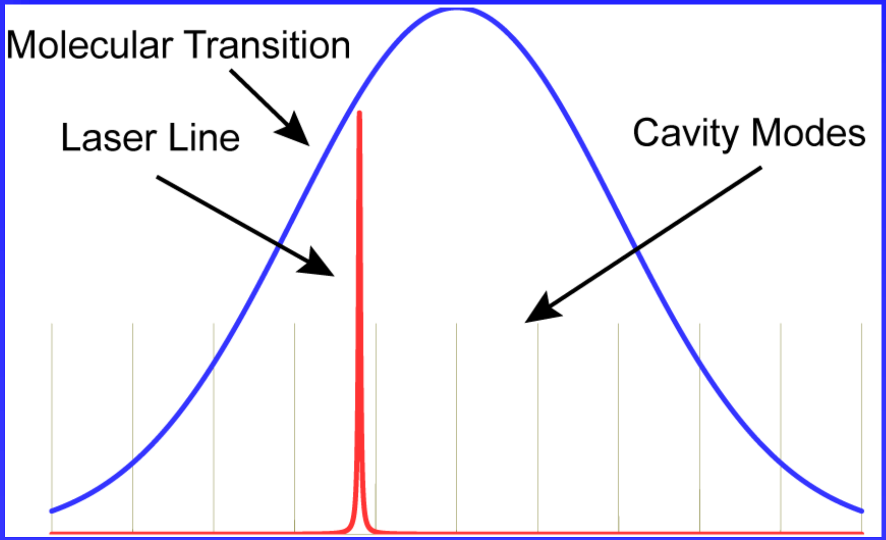


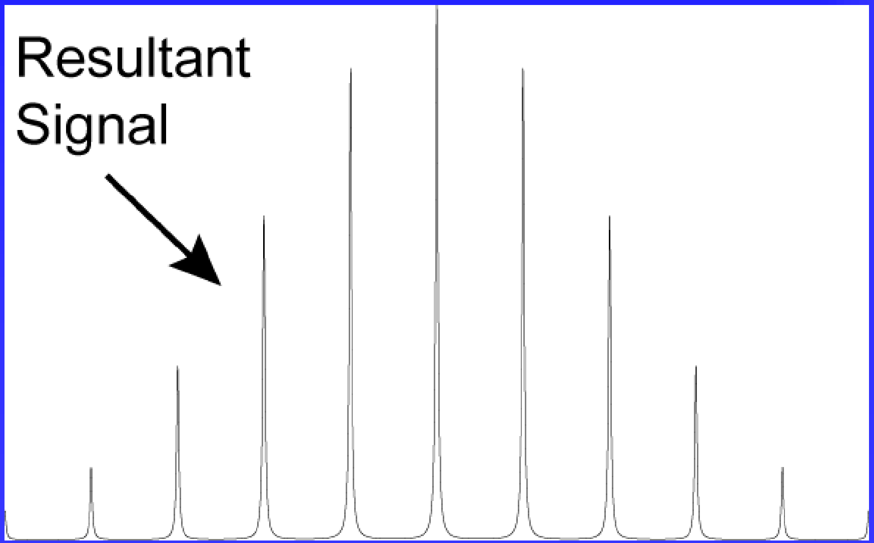
Cavity Mode Examples

- For a 1m cavity with 1m radius mirrors at 45 ppm:

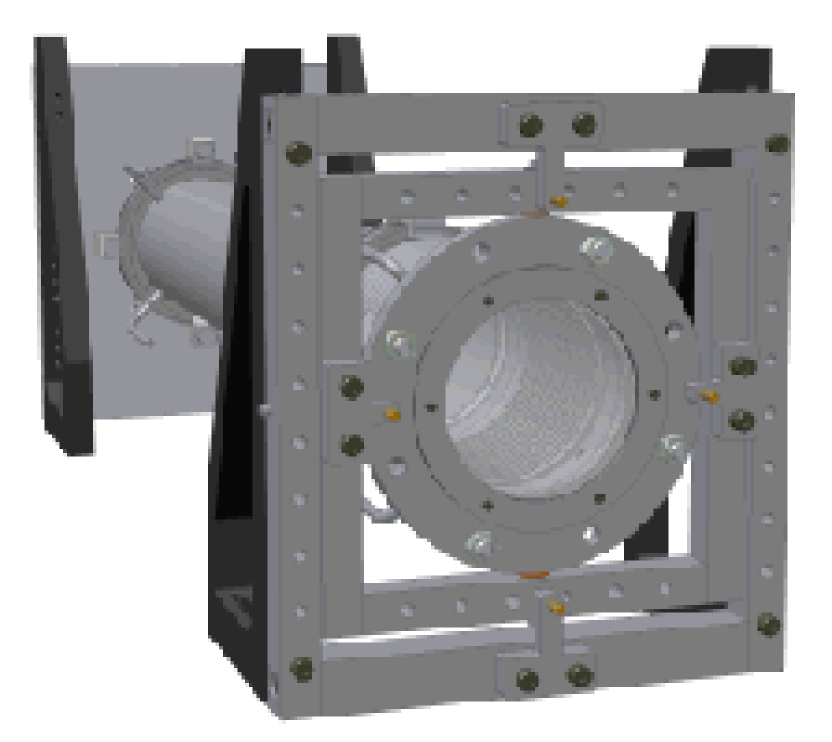
$$\tau = 75\mu s \qquad \Delta\nu_{\text{mode}} = 150 \quad MHz \quad (0.005cm^{-1})$$

$$\Delta\nu_{\text{FWHM}} = 2 \quad kHz \qquad \Delta\nu_{00\rightarrow 01} = 75 \quad MHz$$





Ways to decrease spurious coupling to cavity resonances



New 4” ICOS cell under construction

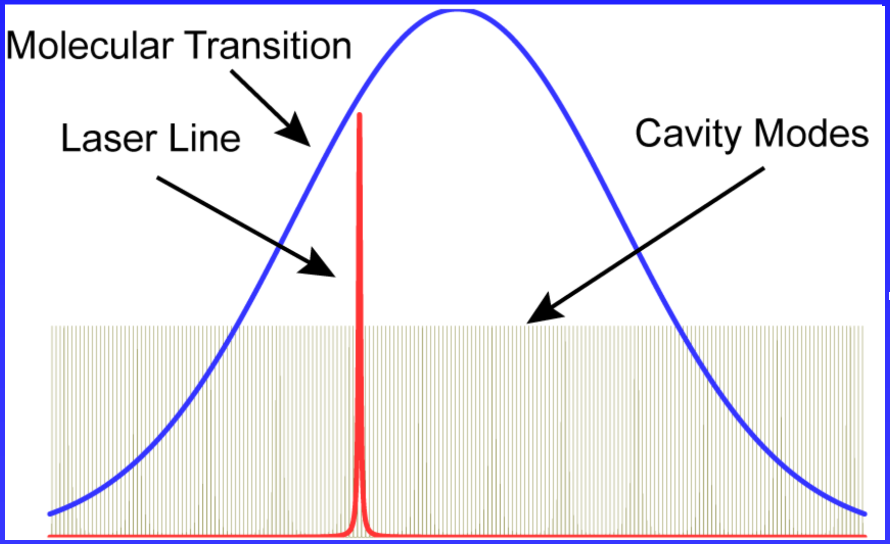
- Off-axis alignment to minimize mode noise
  - Collapses mode spectrum by allowing many passes before reaching re-entrant condition.
- Moving the mirrors to blur the mode spectrum
- Broaden the laser line to prevent coupling to a single resonance

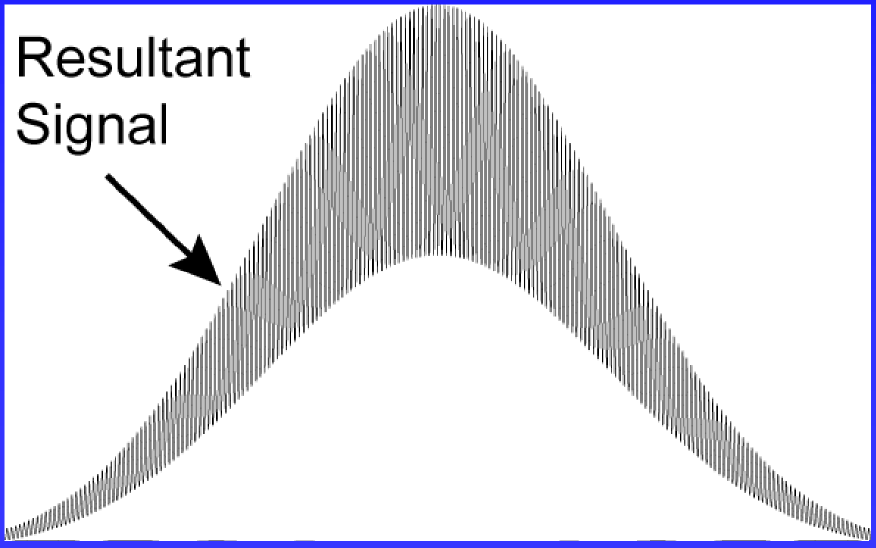
Example of Off-Axis Mode Spectrum:

- For a 75cm cell, 6m mirrors, 180 ppm & 100 Passes:

$$\tau = 14\mu s \qquad \Delta\nu_{\mathrm{mode}} = 2 \quad MHz \quad (0.00007cm^{-1})$$

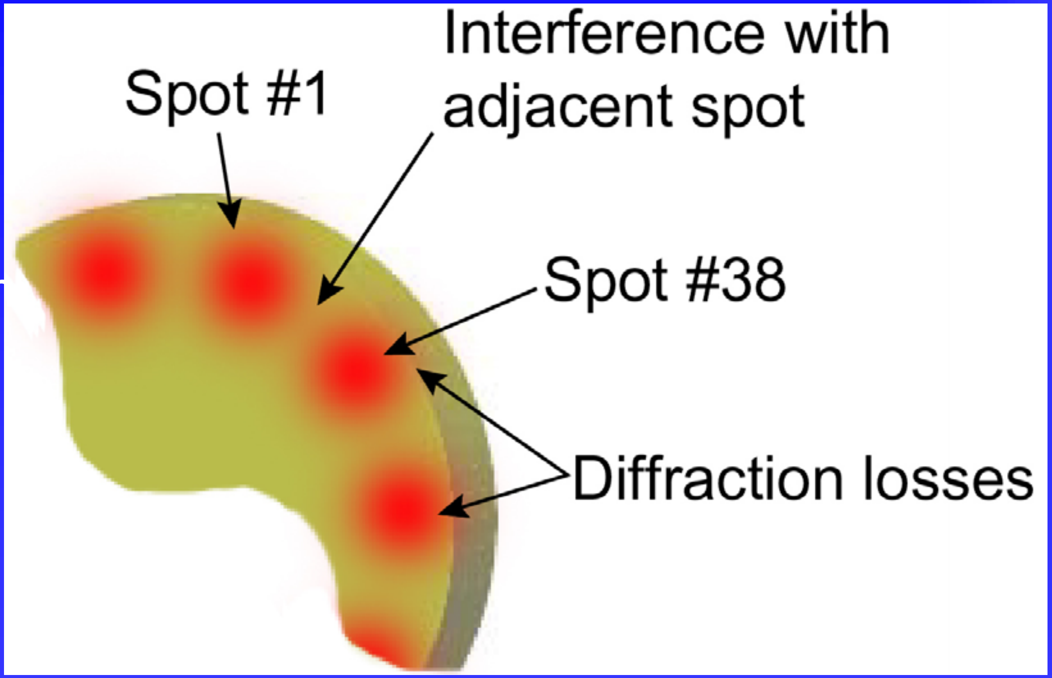
$$\Delta\nu_{\mathrm{FWHM}} = 11 \quad kHz \qquad \Delta\nu_{00\rightarrow 01} = 100kHz$$





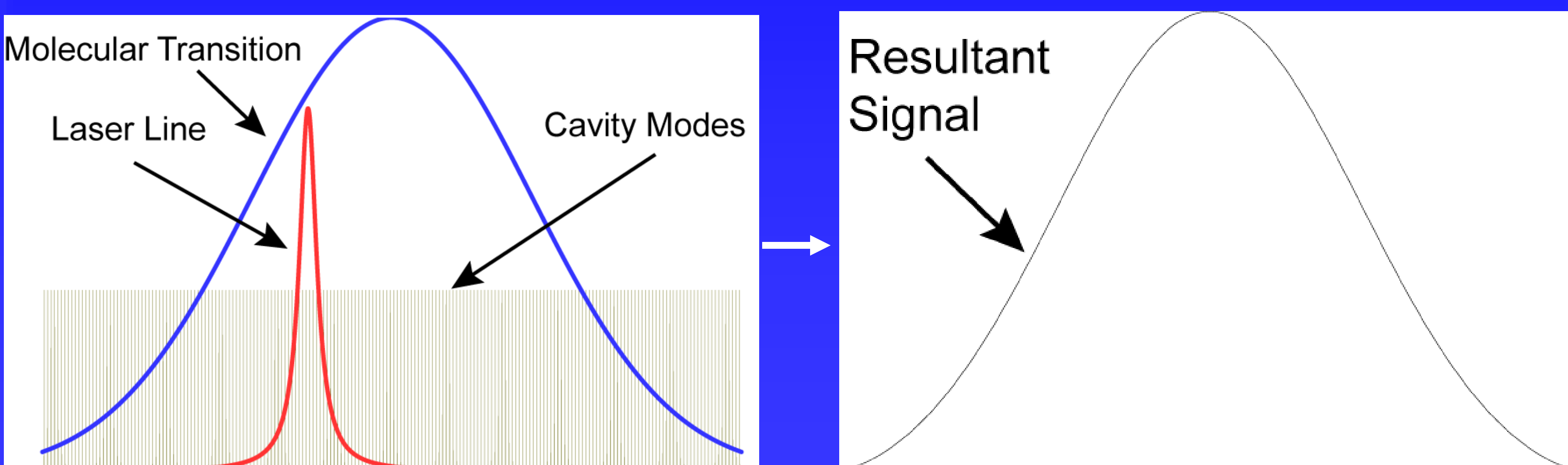
Remaining problems

- Off-axis alignment to minimize mode noise
  - Puts beams nearer to the edge of the mirrors
  - Some “tails” of the beams may overlap and interfere before the reentrant condition is supposed to be reached.



Broadening the laser line to reduce coupling to cavity resonances

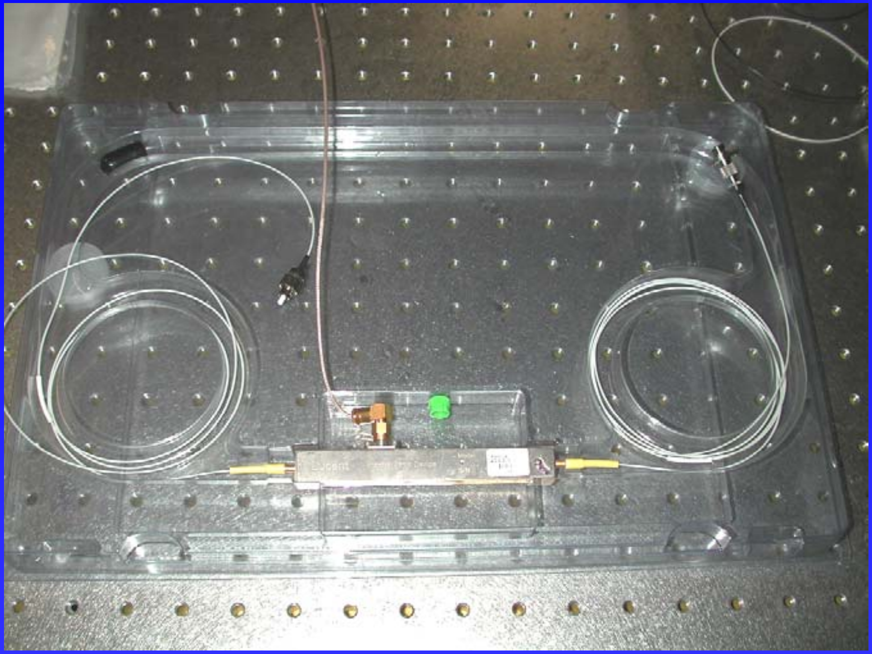
- Changing the laser linewidth
  - Broadening the laser linewidth to excite many cavity modes at once will reduce the coupling to any given mode
  - The laser can not be allowed to feedback from the cavity
  - Laser must still be narrow compared to molecular transition.
  - Ideal Situation:



How do you broaden the laser?

- QCL/DFB: Change the quality of the Bragg Grating
  (feasible in the NIR and Mid IR)

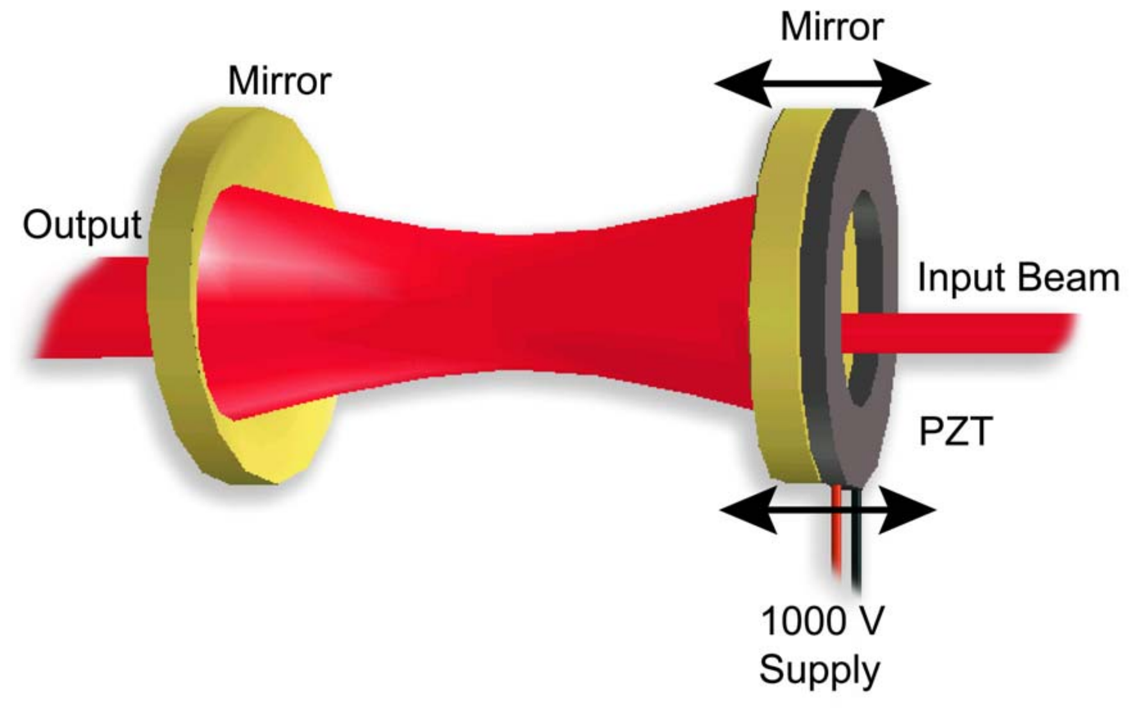
- Modulate the light
  - EOM for phase, amplitude or frequency Modulation
    (feasible in the NIR)
  - Current Modulation for Frequency modulation
    (feasible in the NIR and Mid IR)



Moving the Mirrors to Reduce Couping to Cavity Resonances

- Moving the mirrors
  - Moving the mirrors on the order of the time constant of the cavity should be able to “blur” out the cavity modes by changing the quality of the resonator without significantly changing the reflectivity.

- Distortion of the curvature of the mirror surface will need to be investigated
- Heat dissipation may be an engineering challenge
- High voltage supplies will be needed
- Bonding PZT to mirror may be difficult

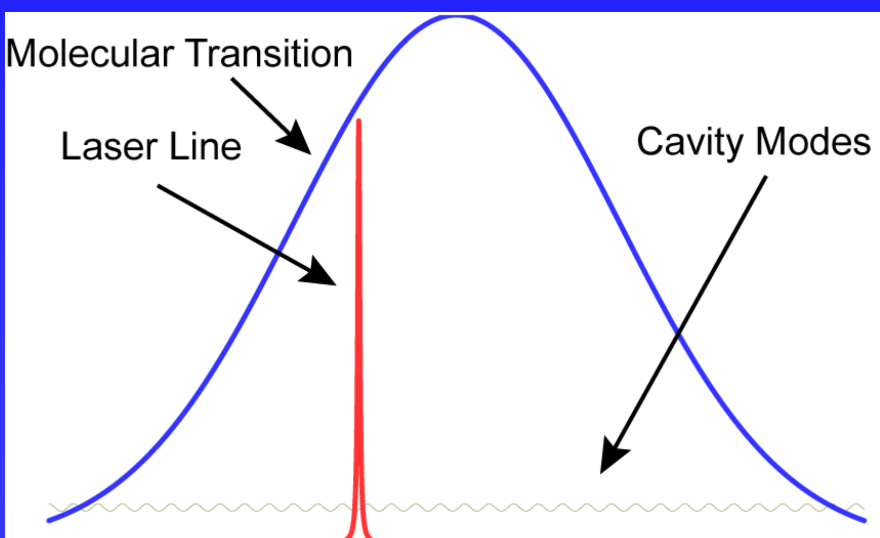


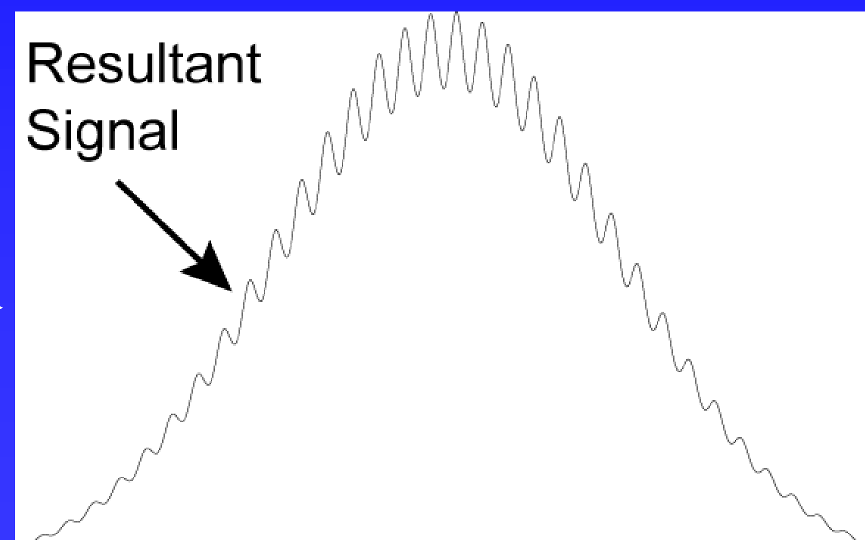
"Blurred" Mode Spectrum:

- For a 75cm cell, 6m mirrors, 180 ppm:

$$\tau = 14\,\mu s \qquad \Delta\nu_{\mathrm{mode}} = 200 \quad MHz$$

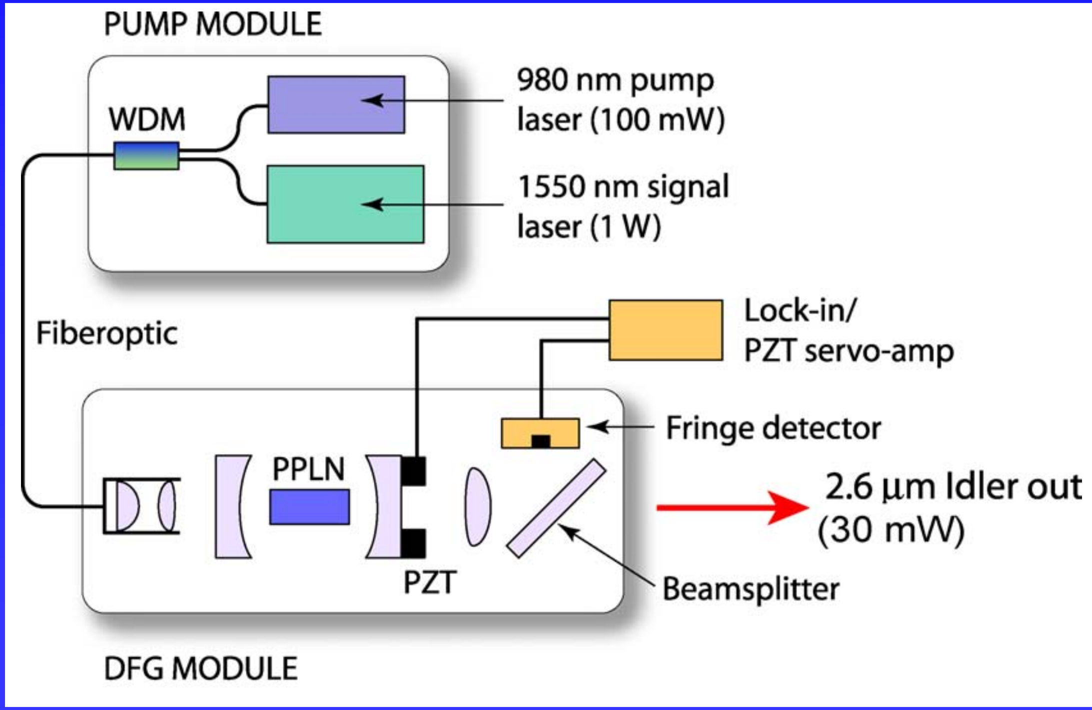
$$\Delta\nu_{\mathrm{FWHM}} = 100\,MHz? \qquad \Delta\nu_{00\rightarrow 01} = 10 \quad MHz$$





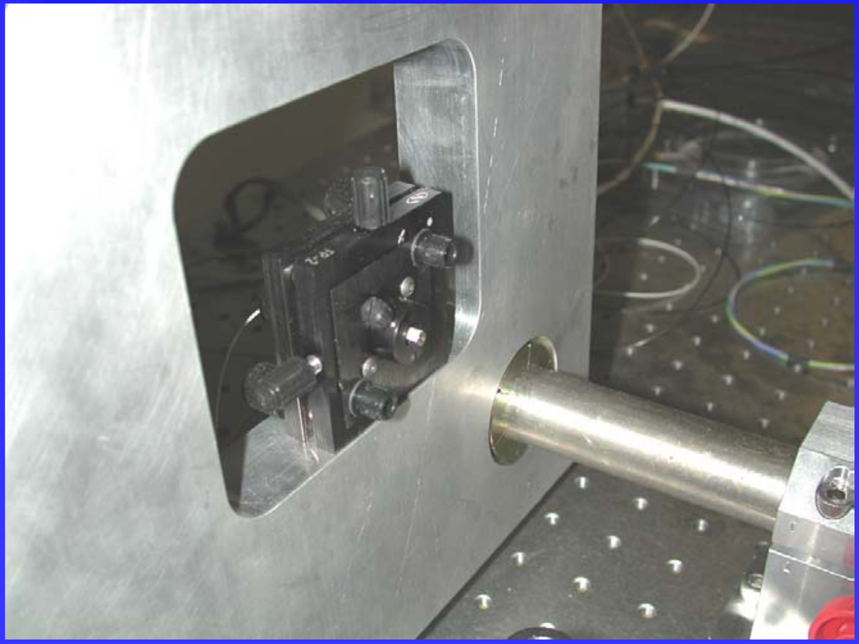
Next Generation Mid-IR light source

- Difference Frequency Generation Lasers (2-4 μm)
  - Benefits:
    - Spectral Qualities of a DFB laser system including tunability and linewidth
    - Built from Fiber Coupled Components
    - Thermoelectric cooling
    - High Power (>25 mW)
  - Demands:
    - Fiber Amplifier
    - Resonant Cavity
    - Single Mode, high power pump laser
    - DFB laser



Cavity Requirements

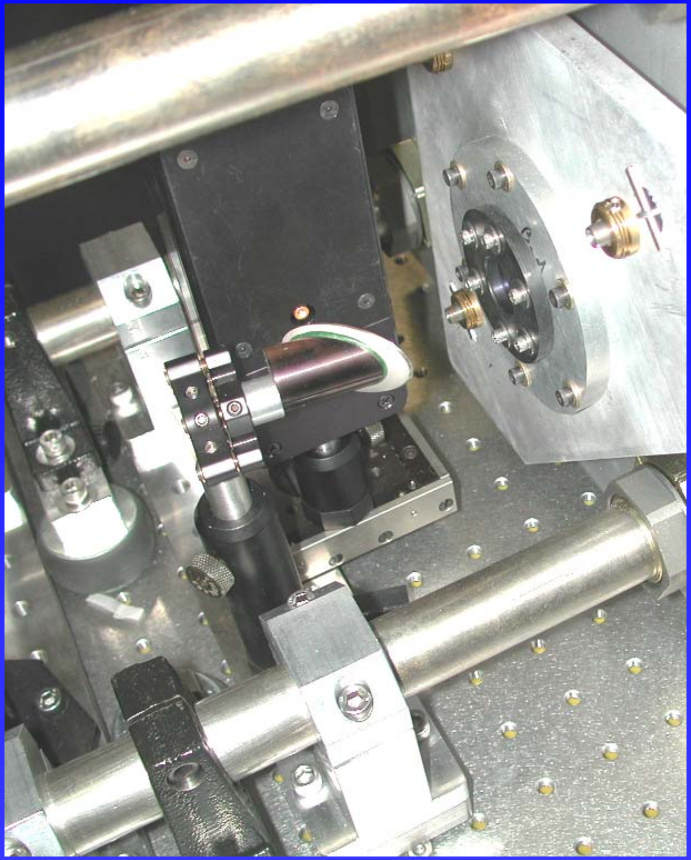
- Stability in Flight
- Stable coupling into the cavity
- Compact



- Vibrational isolation
- Design to allow substitution of lightweight composite parts
- Precise alignment control

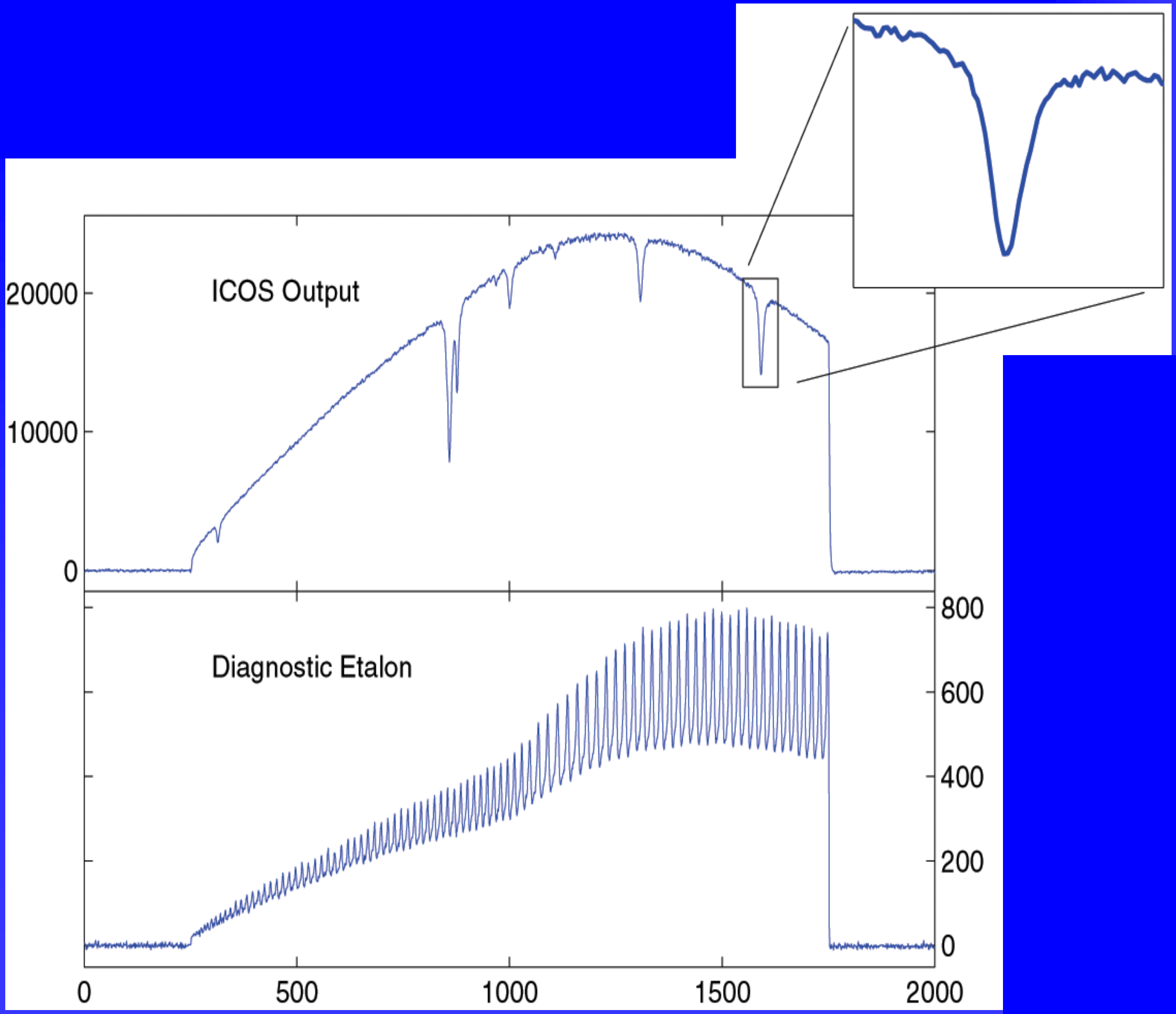
Detection and Acquisition Requirements

- Lower Bandwidth than CRDS
  - 5 Hz – 100 kHz
- No real-time data analysis necessary
- Low noise amplifiers and detectors needed

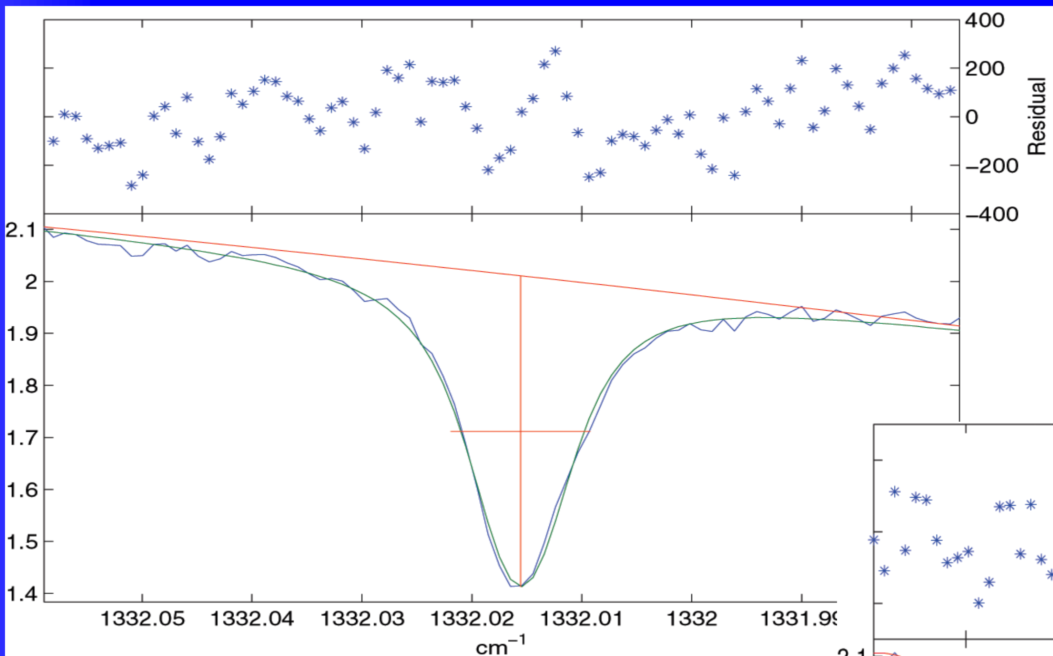


Characteristics of an ICOS Signal

- Signal Characteristics
  - Non-linear tuning rate
  - Complex baseline
  - Skewed lineshapes



ICOS Fitting Results



Standard Fit

– Quadratic baseline

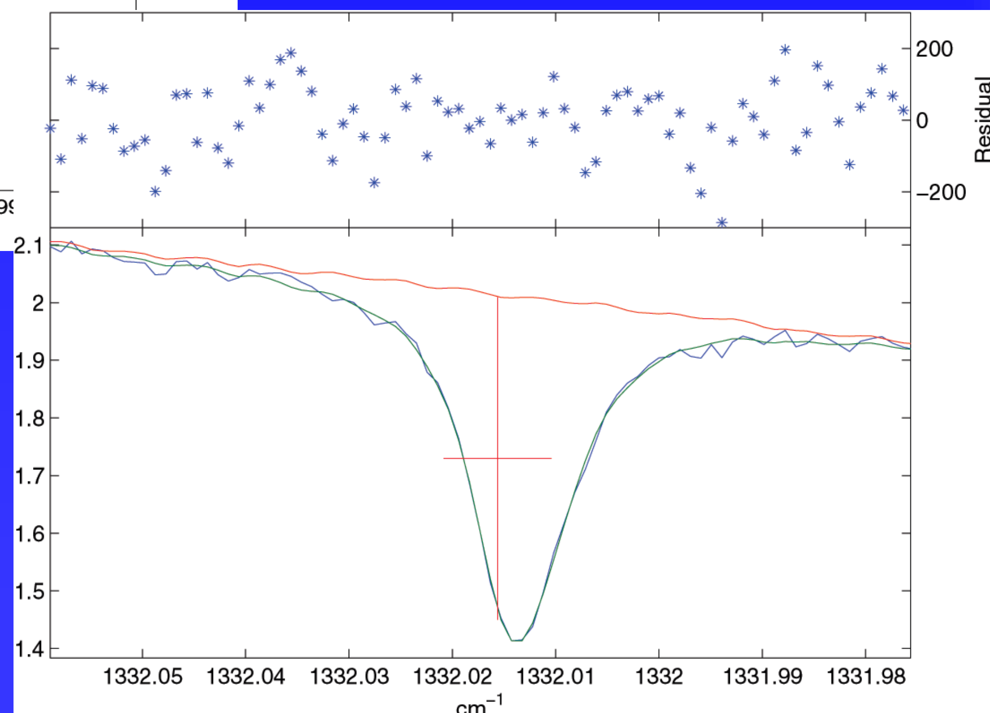
– Voigt lineshape

Improved Fit

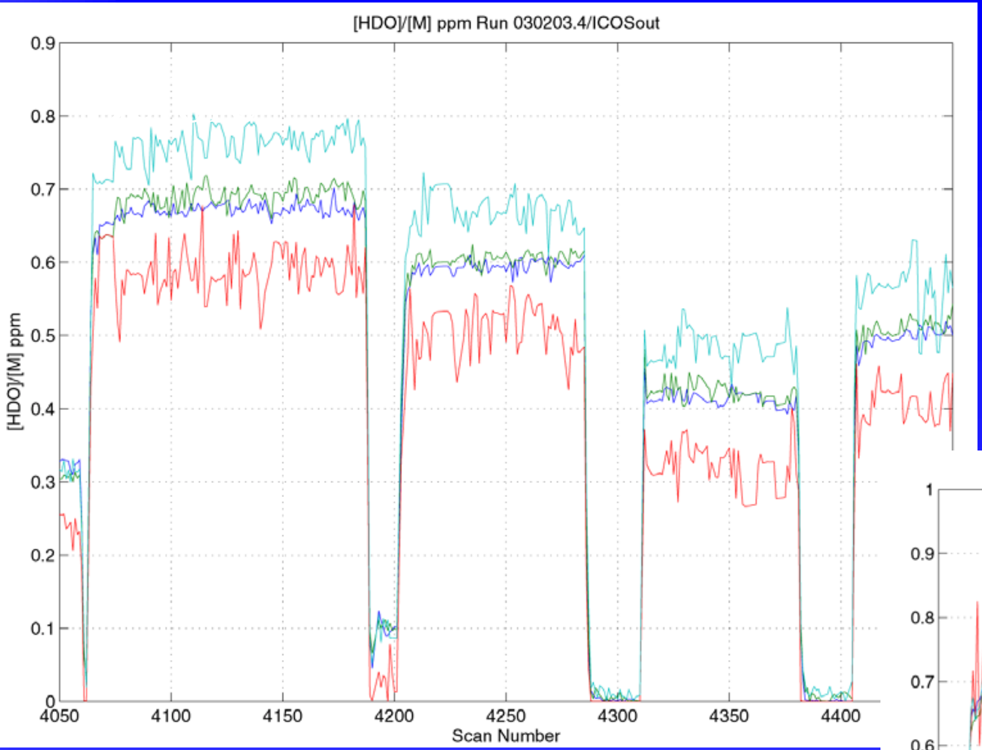
– Singular value decompostion to determine baseline

– Skewed voigt lineshape

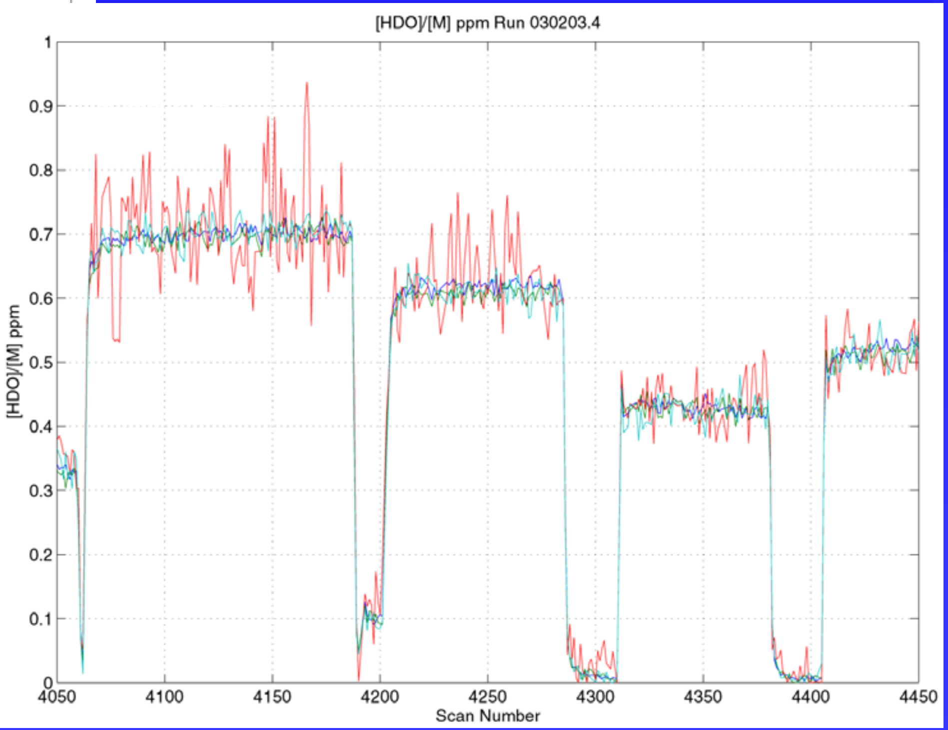
– Nonlinear tuning rate



ICOS Fitting Results



Improved fit results in much better agreement on mixing ratios among HDO lines



ICOS Accomplishments

- Proven reduction in coupling to optical resonances by coupling to the cavity in an off-axis alignment
- Algorithms for accurate fitting of data allowing access to the theoretical sensitivities of ICOS
- Control software complete for both NIR and QCL ICOS spectrometers
- Construction of optical cavities for ICOS Spectroscopy
- Implementation of QCLs for ICOS spectroscopy
- Adaptation of NIR diodes to ICOS spectroscopy
- Adaptation of NIR electrooptic modulator for spectroscopic use, including all necessary driving circuitry
- Construction of mirror coatings to have reflectivity at visible wavelengths (for alignment) and mid IR wavelengths (for spectroscopy)

Areas for Future ICOS Research

- Investigation of the effects of changing laser linewidth through modulation
- Reduction of spurious coupling to cavity resonances by using PZTs to move mirrors
- Continued investigation of sampling concerns inside optical cavity
- Implementation of improved detector and preamp circuitry
- New revision of QCLI to allow more flexibility, higher duty cycle and lower noise

Acknowledgements

- Funding
  - NASA IIP Program
- Research
  - James G. Anderson
  - Frank N. Keutsch
  - Elizabeth J. Moyer
  - Larry Lapson
  - David Sayres
  - Jesse Kroll
  - Norton Allen
  - Joe Demusz
  - Mike Greenberg